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diagrams in the hope that the latter ~~will~~ provide evidence of the mode of origin of the rocks concerned. Such papers are useful in summarizing the available sources of data and presenting a first approximation to the chemical characters of a province, and they are much more useful when (as is not always the case) the analyses are given in full. But it is certain that all this work will sooner or later have to be repeated with due attention paid to the rarer constituents. The " petro-chemist " has in too many cases been content to reap a thin crop from the whole field instead of attempting to extract a full harvest from the more fertile areas.

In those investigations where the significance of geochemical detail has been fully appreciated the immediate rewards in discovery have been correspondingly ample. This is made abundantly clear by Dr. Groves in a welcome chapter which contains an able review of the widely scattered data concerning what is already known of the geochemical distribution of elements. As his summary is the first of its kind to appear in English it should be a stimulating revelation to those chemists and petrologists who have not followed the recent geochemical literature of other countries. Stimulating, because so much still remains to be done.

Analyses of rock-forming minerals are required in order to ascertain the mineralogical location of the rarer dispersed constituents of rocks. It is worth while to compare the enormous number of words made out of 26 letters with the relatively small number of minerals made out of 92 elements. Many of the rarer elements are dispersed in common minerals and it is a worthy task for the chemist to search for these hidden elements, so that the principles of their geochemical associations may be discovered.

To take an example, little is known of the distribution of strontium in minerals. Yet strontium is a more abundant element than zirconium, notwithstanding the fact that zircon is an easily recognized accessory in many rocks. The characteristic concentration of zirconium in a discrete mineral is illustrated by its occurrence in kimberlite, the rock of the diamond pipes of South Africa. Zircon is well known to be present in kimberlite, sometimes in crystals an inch or more in length. Yet Mr. L. S. Theobold, who is the

first analyst to have made a thoroughly detailed analysis of kimberlite, was unable to find a measurable amount of ZrO_2. The reason becomes clear when the proportion of zircon in kimberlite is considered. Data provided by Professor S. J. Shand show that this proportion must be less than 0·0025 per cent. Thus the fact that ZrO_2 was not determinable in a particular sample of kimberlite indicates that zirconium is not dispersed through the rock, but is concentrated here and there in zircon. The same analysis, however, revealed the presence of 0·08 per cent. of SrO. Other analyses show that, while a small part of the SrO occurs in phlogopite and a still smaller part in chrome-diopside, most of it must be dispersed among the vaguely defined ingredients of the groundmass. Many other constituents, such as BaO, Cr_2O_3, V_2O_3, NiO and CuO, are similarly dispersed in rock-forming minerals, so that the petrologist may find no trace of them by microscopical examination. Nevertheless, it must not be assumed that they are necessarily present in smaller amounts than constituents like ZrO_2, which readily reveal their presence by forming specific minerals.

Dr. Groves also serves a useful purpose by pointing out the degree of accuracy which the chemist may reasonably be expected to attain. Some petrologists have questioned the value of determining the rarer constituents on the grounds that the quantities assigned to them by analysts may not be reliable. Again taking strontium as an example, it is of interest to find that the rocks of Eastern Australia are abnormally poor in SrO, whereas those of Southern Rhodesia are unusually rich in this constituent, SrO being frequently even more abundant than BaO. It has, however, been seriously suggested that the difference " in the strontia content of rocks from Eastern Australia and Southern Rhodesia is just as likely to be characteristic of a particular analyst or a particular batch of reagents as of the rocks themselves " (*Geol. Mag.*, 1932, p. 561). That there is no justification for such strictures on analytical methods and reagents was promptly made clear by the spirited replies which this suggestion naturally provoked (*Geol. Mag.*, 1933, pp. 141-144). The present book provides abundant evidence

that, with due care, most of the minor constituents can be determined with ample accuracy for the immediate purposes in view.

Analyses supply the petrologist with accurate data which add precision to his descriptions of the analyzed minerals or rocks and so, in conjunction with correlated and comparative evidence (including analyses of associated minerals and rocks), enable him to interpret the relationships, history and mode of origin of the materials concerned. Even in the less ambitious task of determining and describing rocks, the petrologist may not always find microscopic examination sufficient for his object. This limitation is especially felt when poorly or incompletely crystallized volcanic rocks are under investigation. I have recently had occasion to direct attention to the absence of basalts and olivine-basalts from the volcanic field of Bufumbira in south-west Uganda. I pointed out that it was no matter for surprise to find that "basalts" had previously been recorded from the area, for the simple reason that many of the lavas look like basalts in the field and cannot be confidently distinguished from basalts under the microscope. The first specimen from Bufumbira to be analyzed by Dr. H. F. Harwood was of lava from the crater-rim of Mgahinga: lava which had been described by the late Dr. H. H. Thomas in 1912 as porphyritic olivine-basalt. No better proof could be required that the rock really does resemble basalt. Yet analysis disclosed the presence of 4·09 per cent. of potash. A similar rock from the neighbouring volcano of Muhavura was found by Dr. Groves to contain 4·46 per cent. of potash. These lavas are now more accurately described as shoshonitic absarokite and their affinity to similar lavas occurring in the Yellowstone Park and in south-west Celebes is thus made evident. The absence of basalts from Bufumbira is highly significant from a petrogenetic point of view, since here, as in certain other volcanic areas, wrong diagnoses have fortified the misleading belief that basaltic magmas may have been the dominant source of the various lavas represented.

In the petrogenetic study of crystalline rocks interest is now being increasingly focussed on the processes whereby rocks and magmas have orginated. The nature of the

problems involved has been effectively summed up by Dr. Alfred Brammall in the following sentences: "The study of evolutionary processes, in both the igneous and the metamorphic fields, is the distinctive feature of modern petrology, which seeks to interpret the mechanism of mineral-change, to determine the degree of genetic relationship (if any) between various rock-types in which mineral-transformations have played an important rôle, and to establish the origins of magmas. Its ultimate problems rest in the complex mineral changes which occur on the vague borderline between the igneous and the metamorphic fields—notably those induced in crustal rocks by emanations and exudates from magma" (*Science Progress*, 1936, p. 616).

The migrations and concentrations of elements in ore-deposits are, empirically, already fairly well known. They imply the operation of localized streams of emanations which are often associated with foci of igneous activity. In the evolution of igneous and metamorphic rocks, however, the part played by emanations has hardly been recognized until quite recently. In North America, Europe and the British Isles various independent workers are now finding widespread evidence in the crystalline rocks of migrations of elements on a hitherto unsuspected scale. There is here an unprecedented opportunity for the analytical chemist, since, without his aid, the petrologist can form only a qualitative idea of the more conspicuous compositional changes represented by the mineral replacements and other alterations which he detects in the field and under the microscope.

A particularly clear and convincing example of the transformation of quartzite into igneous rocks by emanations has recently been described by Miss Doris L. Reynolds (*Min. Mag.*, **24**, 1936, pp. 367-407). The processes responsible for such transformations may be conveniently referred to by the term *transfusion*, since they involve the intimate migration of highly energized matter into pre-existing crustal rocks which are thereby metasomatized and, in some cases, mobilized and turned into magma. Fusion of crustal rocks implies no more than the addition of energy; transfusion implies the addition of energized material from a flux of emanations. The rocks representing the transfusion

phenomena described by Miss Reynolds are exposed on a spectacular scale at the north end of Kiloran Bay in the Hebridean island of Colonsay. In the marginal zones of three intrusions of dark green hornblendite innumerable blocks of white quartzite occur which can be seen in all stages of metasomatic replacement by micropegmatite, syenite and appinite. In places the process of transfusion led to the generation of magmas of syenitic and appinitic composition, as witnessed by the occurrence of veins which can be traced from the felspathized quartzite contacts where they originated. The evidence is complete that metasomatism and magma formation are intimately related processes.

Chemical analyses of the quartzite and the products of transfusion show — as regards the dominant elements — that the earlier emanations introduced sodium, potassium and aluminium, with production of micropegmatite and syenite, and that the later emanations introduced calcium, iron and magnesium and so produced the hornblende and chlorite of the appinite. For further details, and particulars of the migration of the less abundant elements, reference should be made to the original paper. The point of immediate interest, however, is not to demonstrate petrogenesis, but to illustrate the necessity for analyses. No analyses would normally be required for the identification of such rocks as hornblendite, syenite and quartzite. But analyses of carefully collected *series* of related specimens are obviously essential in order to ascertain the composition of the materials introduced at various stages by the flux of emanations. The conception of the flux of emanations is a new one in petrology, and one that opens up entirely new vistas of co-operative research. Its recognition makes increasingly evident the fact that both geochemistry and petrology are being steadily enriched by discoveries which lie in territory outside the fields of knowledge so far explored by the physics and chemistry of the laboratory.

In conclusion I should like to express my appreciation of the invitation to write a Foreword to this book. It has provided an opportunity not only for commending the book itself, but also for discussing the question, so often asked, why petrologists are dependent on chemical analyses, as well

as on field and microscopic work, for the progress of their investigations. Both geochemistry and petrology have now reached a stage in their development when more analyses, and more detailed analyses, are required than ever before. The time is therefore peculiarly appropriate for the appearance of just such a book as Dr. Groves has written.

SCIENCE LABORATORIES,
THE UNIVERSITY,
DURHAM.

November 28, 1936.

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CHAPTER I

THE LABORATORY : ITS EQUIPMENT AND APPARATUS

THE first essential of the laboratory is that it shall be large enough, be adequately ventilated, and equipped with an efficient fume cupboard, so that the health of the worker is not affected by fumes, particularly those of hydrofluoric and sulphuric acids. Equipment of the laboratory will, of course, depend on the geographical situation and on the funds available. It must not be thought that a highly equipped laboratory is essential for good results. The author has worked in one in Central Africa where there was neither water, gas nor electricity laid on, yet all these difficulties were successfully overcome and satisfactory analyses were made.* Suggestions for overcoming such difficulties are given at the end of this chapter.

Points to which special attention must be paid are :

(a) Necessity for a good balance.
(b) The use of best quality reagents, including those of A.R. standard where necessary.
(c) Possession of sufficient platinum vessels of suitable size.
(d) Use of best quality glassware and ashless filter papers.

With regard to the laboratory itself, at least one outside window is necessary so that colorimetric comparisons may be made in daylight. The laboratory should be well lit by both windows and artificial light. Too many windows and doors, however, may lead to draughts, causing burners to strike back, small luminous flames to direct their heat anywhere but on the required spot, and there is always the risk of losing material from light residues in uncovered

* *Cf.* H. S. Washington, "The Chemical Analysis of Rocks," New York, 1930, p. 29.

crucibles. While some of these difficulties may be obviated by protecting the burners from draughts with small boards of asbestos fibre (such as "Uralite"), it is better that the ventilation be carried out by means of large diameter pipes connected to a powerful electrically-driven suction-fan. One or more ejector fans fitted to the tops of windows are useful aids to ventilation, are easily fitted, and are cheap to run. There should be six gas taps, one sink, and one electric power plug for each worker.

If steam can be laid on, it will prove a most valuable asset and enable evaporations to be carried out in safety overnight, thus greatly expediting the work. The best place for the jets is in the fume cupboard, but only a very slight escape of steam is necessary. The steam, for which a suitable pressure is 15 lb. per sq. inch for stills, and 3-4 lb. per sq. inch for steam-baths, may also be used to heat a combined oven and still, or the latter may be heated electrically. A gas-heated still introduces unwanted fumes and heat into the laboratory atmosphere. A copper still (tin lined) is essential and the purity of the water produced should be tested from time to time.

One fume cupboard should be assigned to operations involving the use of hydrofluoric acid. The glass in this cupboard will soon be badly attacked and the coating which forms on its inner surface will require to be scraped off at intervals of several months, otherwise it tends to flake and fall into evaporations in progress. The frequent evaporations of hydrofluoric acid with sulphuric and nitric acids are carried out in this cupboard on sand-baths over small flames. It is very convenient, particularly if more than one person is working in the laboratory, to use a large sand-bath in the cupboard in place of smaller ones. This is made by cutting out an 18-inch square of thin sheet-iron, and turning up the edges $\frac{1}{2}$ inch all round. The bath is supported at its corners on tripod stands and a large gas ring is placed under the centre. The gas burner is kept burning at full pressure, the variation in temperature for each stage of a particular evaporation being attained by moving the dish towards or away from the centre. After a few evaporations the correct positions are soon learned, but it is wise to err

somewhat on the cool side rather than to overheat the mixture with consequent spurting — a danger to both the novice's analysis and his face.

Ordinary bunsen-burners are used, but for most purposes they should be fitted with a star-support and cone. Teclu burners are used where a higher temperature is required. A blast Méker burner is essential for certain operations requiring the highest temperature, the air being supplied by a small blower directly coupled to an electric motor. A quite small and inexpensive outfit will suffice if one burner only is to be used. A ¼ h.p. electric motor with a belt drive to a somewhat larger blower will provide ample air pressure for three large Méker burners ; in this case some piping and taps will be required along the bench. Such a blower should never be made to work against closed taps as the back pressure becomes too great and may damage the blades ; it is better to leave the air taps open and control the air pressure by the speed of the motor. By combined use of the rheostat controlling the motor, the gas tap, and the air gap on the burner, all possible variations in the size and type of flame may be obtained. A spare tap on the air pipe will be found very useful for drying out flasks, absorption tubes, etc.

For convenience in the reduction of the total iron solution, a carbon dioxide cylinder, with a suitable length of rubber tubing, is fixed between a gas burner and a neighbouring sink. After boiling and reduction, the flask may be cooled under the tap without interruption of the current of carbon dioxide. The cylinder, conveniently fastened in an upright position to the edge of the bench by a belt of leather or webbing, should be fitted with a fine adjustment. In addition to iron reductions, this arrangement will be ready for the expulsion of sulphur dioxide after the reduction of vanadium, and the preparation of air-free water saturated with boric acid for ferrous iron determinations.

The supply of water-baths should be such as to allow of the use of two or three at a time by each worker, who also requires one copper water-bath fitted with a porcelain top having four round holes varying from 1½-3½ inches in diameter. In addition, one or two 6-inch copper water-baths

fitted with a set of porcelain rings will be required. Water-baths should have a constant-level attachment fitted, and have porcelain instead of copper rings to avoid staining platinum dishes. The baths may be heated by gas or electricity. The latter is to be preferred on account of its cleanliness, absence of corrosion, and the way in which the fur formed is thrown off by the interior heating coil and is thus easily removed by hand. For sulphur determinations the use of either a steam jet or electrically heated bath is essential. The greatest advantage of a water-bath fitted with an interior electric heater is that it may be left running overnight without risk of fire. Nowadays the heating elements supplied for these baths have a cut-out incorporated in them so that, should the water supply fail, the current is stopped automatically before an excessive temperature is reached. Such heaters are sold separately so that a gas-heated water-bath may be readily converted to an electrically heated one with a resultant improvement in the laboratory atmosphere. A 6-inch bath usually requires a 650-watt heater, and a 12-inch bath one taking 1,000 watts. Boiling point is reached in fifteen to twenty minutes. Electrically heated water-baths with cut-outs incorporated form a most efficient substitute for steam jets.

A mechanical stirring apparatus is useful, particularly in the determination of strontia, but it is not essential.

The supply of platinum apparatus should be as liberal as possible since upon it depends the volume and speed of the work turned out. The author considers one 25 g. crucible with lid, one 20 g. thin dish, a 4- or preferably 6-inch dish, and one stirring rod should constitute the minimum outfit.* With this only one analysis can be done at a time and then not very quickly. In cases where a large dish is not available, its place may be taken in silica estimations by a porcelain one (with a black inner glaze) and, in the large evaporations for alkalis, by a silica dish.

A practical set for a person doing one analysis at a time would be : one 35 g. crucible and lid (for main fusion and

* With platinum at £7 an ounce this outfit would cost £50 to £70, but it is possible to hire these articles from the leading suppliers of platinum apparatus. (The late 1950 price was around £30 per oz.)

ferrous oxide), one 20 g. crucible and lid (ignitions), one 20 g. dish (final evaporations of alkalis, etc.), one 3-4 inch (many uses), one 6-inch dish (for silica and alkalis). An even larger but shallow platinum dish of 7-8 inches diameter, capable of taking 600 c.c. of liquid, affords a considerable saving of time in the determination of the alkalis. If analyses are to be carried out three or four at a time, then the number of both the small crucibles and 3-inch dishes will each have to be increased to three or four, with a corresponding number of stirring rods.

A Munroe crucible (a platinum crucible fitted with a mat of precipitated platinum) is more rapid in filtration than a fritted glass filter and maintains a much more constant weight. It is not essential, however, and its place may be taken by glass filters. A platinum boat may be required occasionally in cases where a rock or mineral will not give off the whole of its water at a red heat, but for ordinary rock-analysis it will very rarely be required.

A steel pestle and mortar, as described on p. 18, or a large-size diamond mortar, together with a hammer or mallet, will be required for crushing rocks and minerals. A suitable stand or block is also described on p. 19. An agate pestle and mortar will be required, especially for grinding and mixing the reagents for the determination of alkalis. It should be sufficiently large to be able to do this without loss (*i.e.*, not less than 4 inches in diameter).

For the rest, little more than the usual laboratory apparatus will be required. The glassware should be of the most resistant type, such as " Pyrex," which is a boro-silicate glass. The best quality " ashless " filter papers should be used. Suitable grades and sizes are Whatman's No. 40, 7 cm., 9 cm., 11 cm., 12·5 cm. and 15 cm., and the same sizes in the No. 41 grade. For the determination of chromium and vanadium, the special No. 54 12·5 cm. will be required. A few toughened tips will also be useful (see p. 131).

The balance must be housed in a separate balance room away from the effects of corrosive fumes. A good analytical balance is required capable of weighing to 0·1 mg., and a convenient sensitivity to which it may be set is 25 (*i.e.*, a change in the position of the rider equivalent to 1 mg.

displaces the position of rest of the pointer by 2·5 scale divisions).

Laboratories without Usual Supply of Gas or Water

If the laboratory is far removed from a town, or is situated in the tropics, some or all of the usual services of water, gas and electricity may not be available. Nevertheless, provided that pure chemicals, platinum apparatus, a good balance, and a simple laboratory equipment are available, satisfactory work may still be done though at somewhat reduced speed. In the absence of a constant water supply, rain-water from the roof may be stored in a large tank arranged at such a height that there will be several feet of head for the taps. It is advisable that such a tank be covered and the entrance fitted with a trap. Under these conditions the efficiency of the filter pumps is greatly reduced, but nevertheless the pressure will usually be sufficient to work a Munroe crucible, which filters much more readily than one of fritted glass.

Provided one has an assistant to do the preliminary heating of alcohol, paraffin, and petrol burners, to attend to them and keep them clean, the absence of a gas supply does not present such difficulties as at first might be supposed by a person accustomed to this convenience. In some parts of the tropics where sugar is grown, alcohol is cheaper than paraffin or petrol and in such places alcohol bunsen burners will be largely used. They are procurable in several sizes, of which the medium is the most useful. They need to be protected from draughts, otherwise they tend to cool off, when liquid alcohol flows out and sets fire to the bench.* Against this they require no pumping, the height of the flame can be regulated by a valve, and they never give a sooty flame which will damage a platinum crucible. Glass spirit lamps are extremely useful, but tend to crack when used under ovens or water-baths.

For higher temperatures where the gas Teclu burner is usually employed, a paraffin or petrol blow-lamp is the best substitute. An ample supply of prickers for cleaning the

* The large burners tend to cool off more than the smaller ones.

jets should be kept, for the efficiency of these burners depends on the cleanliness of the jets and the freedom of the fuel from dirt particles. In some parts of the world it will be necessary to filter the fuel before use. When using platinum, these burners cannot be left unattended for more than a minute or two, for the flame may become sooty either through diminished pressure or partial obstruction of the jets by dirt. Copper stills can be obtained suitable for heating over a paraffin burner of the " Primus " type. The use of these alcohol, paraffin or petrol burners renders essential the presence in the laboratory of a fire-extinguisher.

Excellent gas-producing plants are now available for use with either paraffin or petrol, but the capital expenditure is rather heavy and burners of special type may be required.

CHAPTER II

REAGENTS

It is manifest that the accuracy of silicate analysis, as indeed any branch of analytical chemistry, is dependent, among other things, on the purity of the reagents employed. It is useless to seek small quantities of chloride, sulphate, phosphorus, barium, strontium, nickel, chromium, vanadium, etc., if these are present in the reagents ; indeed, it is worse than useless for the results will mislead other workers. In some cases it is not possible, on technical and economic grounds, to produce reagents absolutely free from undesirable impurities. Thus the calcium carbonate used in the determination of the alkalis will always be found to contain alkalis. Even with calcium carbonate of A.R.* quality the alkali content is appreciable. In such cases a determination for the content of the particular impurity in the reagent (known as the " blank ") has to be made. If the blank is too high, it is advisable to reject the material. Wherever determination of the blank is necessary it will be indicated in this chapter. The growing tendency, nowadays, for A.R. chemicals to be manufactured with a guarantee that they conform to definite standards, the limits of various impurities being listed on the bottle, is of great assistance, but even guaranteed reagents should not be taken on faith.

The reagents will be listed first, and then the various wash liquids, with instructions for their preparation, will be given in a separate list, as it is convenient to make these up before commencing a series of analyses. The quality of the reagents will be indicated by the usual terms " A.R.", " pure ", " recrystallized ", etc.

* Analytical Reagent.

List of Reagents.

The following list covers the requirements for the methods of general application only. The quantities given are for a laboratory with one or two workers.

Hydrochloric acid. Pure. 1 Winchester.
Hydrochloric acid. Commercial. 1 Winchester. For generation of hydrogen sulphide and cleaning.
Nitric acid. Pure. Special. 1 Winchester. This should be tested to ascertain its freedom from chloride.
Nitric acid. Fuming. Sp. gr. 1·50. 1lb. Required for strontia determination only.
Sulphuric acid. Pure. 1 Winchester.
Hydrofluoric acid. Redistilled. (Supplied in 1 lb. paraffin-wax bottles). This is suitable for general usage — *e.g.*, decompositions — but not for the silica determination.
Hydrofluoric acid, A.R. (in 1 lb. paraffin-wax bottles), is used for the silica determination. The blank for non-volatile residue should be determined.
Cleaning acid. Commercial chromic acid in strong sulphuric acid.
Chromic acid. Pure. Required for the wet combustion of carbon, etc.
Phosphoric acid. Syrupy. 1 lb.
Perchloric acid. 65 per cent. A.R., 1 lb., is used for the preparation of the 20 per cent. acid for alkali determinations, and at full strength in conjunction with hydrofluoric acid for certain decompositions.
Perchloric acid. 20 per cent. is made from 65 per cent. acid.
Boric acid. Powder. 1 lb.
Boric acid. A.R. 4 oz. This must be free from phosphorus and is used only for phosphorus determinations.
Citric acid. Pure. 4 oz.
Acetic acid. Glacial. 2 lb.
Ammonia. Sp. gr. ·880. 1 Winchester. This is generally used diluted to 1:2 or 1:3. The ammonia water should be tested with calcium chloride to insure its freedom from ammonium carbonate, which would cause co-precipitation of lime with the alumina.
Hydrogen peroxide. 20 vols. 1 lb.
Caustic soda. Pellets. 1 lb.
Caustic potash. Pellets. 1 lb.
Sodium carbonate. A.R. 1 lb.
Fusion mixture. A.R., 4 oz., will be used only for the fluorine and sulphur determinations.
Calcium carbonate. A.R. 1 lb. The blank for the alkali content must be determined as described on p. 79. The purchase of several pounds of this reagent will mean that the blank, once determined, need not be repeated while the supply lasts, which will probably be several years.
Ammonium carbonate. A.R. 1 lb. Preferably supplied in small cubes. Four or five of these are dissolved for each alkali determination, and will be sufficient for both lime precipitations.
Ammonium phosphate. A.R. 1 lb.
Ammonium chloride. A.R. ½ lb.
Oxalic acid. A.R. 1 lb. The solution is to be made as needed.
Ammonium oxalate. A.R. 1 lb. For lime precipitations.
Ammonium oxalate. Recrystallized. 1 lb. This will be required only for making up the wash solution.
Ammonium nitrate. 1 lb. This will be required only for making up wash solutions and in 50 per cent. solution used for phosphorus.

Sodium acetate. A.R. 4 oz. This will be needed for those occasions when the basic acetate method has to be used — *e.g.*, when manganese amounts to several per cent. or more, and principally in the analysis of minerals, meteorites, etc., where there is appreciable nickel, or cobalt.

Sodium pyrosulphate. Pure. 1 lb. This must be fused salt and should be kept as dry as possible.

Potassium nitrate. 4 oz. A small bottle of this will last a long time, since only a few crystals will be used for each analysis.

Potassium chromate. 1 oz. Under normal conditions only a few grams will be required in the course of as many years.

Potassium permanganate. 1 lb. A.R.

Silver nitrate. 4 oz. Pure.

Ammonium molybdate. Recrystallized. 8 oz.

Barium chloride. A.R. 4 oz.

Potassium titanofluoride. 1 oz. Pure.

Magnesium chloride. Pure. 1 lb.

Potassium periodate. 1 oz. This is an expensive reagent, but only 0·1-0·2 g. will be used for each manganese determination.

Potassium perchlorate. 4 oz.

Bromine water. 1 lb. This should be saturated and made from pure bromine.

Mercurous nitrate. This will be used only in the determination of chromium and vanadium.

Zinc oxide. 4 oz. A little of this is needed for each fluorine determination.

Ferrous sulphide. 7 lb. This will be required solely for the generation of hydrogen sulphide.

A cylinder of carbon dioxide. A small (10 cubic feet) cylinder will last one worker a considerable time and is much more convenient than a generator using acid and marble.

A bottle of liquid sulphur dioxide. Required for vanadium determinations; also useful for reducing a manganese oxide suspension.

Calcium chloride. Fused. Granular. 1 lb.

Soda-lime. 1 lb. A useful commerical brand known as "Sofnolite" contains an indicator, so that it is green when fresh but turns pink or brown as its capacity for absorbing carbon dioxide becomes exhausted.

Dimethylglyoxime. 1 oz. A 1 per cent. alcholic solution is used for nickel, so that a little of the solid compound will go a long way.

8-*Hydroxyquinoline.* 1 oz.

α-*Nitroso*-β-*naphthol.* 1 oz. A few g. of this will be required if cobalt is to be determined.

Copper sulphate. A.R. 1 oz. A few g. of this will be required if copper is to be determined colorimetrically.

Sodium diethyl-dithio-carbamate. 1 oz. A 0·1 per cent. aqueous solution is used in the colorimetric method for copper. The solution does not keep for much longer than six weeks.

Alcohol. Absolute. 1 gallon.

Rectified spirit, 95 per cent. 1 gallon. Will be required occasionally, as for the alcohol burner used in the fusion method for total sulphur.

Litmus papers, both blue and red.

Methyl red papers.

Methyl orange.

Methyl red.

Phenolphthalein.

Sand. A special grade of wind-blown sand *with rounded grains* should be kept for polishing platinum apparatus.

Distilled water. Since a considerable amount will be used this is best made on the premises. In any case the quality of the water should be tested from time to time.

Cupferron. 1 oz. This reagent will be needed only if rocks or minerals containing more than approximately 4 per cent. of titania are encountered, when the colorimetric method becomes unsuitable. The salt is kept in a cool, dark place, and the solution is made up as required.

N.B.—In ordering the three common acids and ammonia, it is useful to remember the weight of reagent which is usually put up in one Winchester — *viz.*, HCl 6 lb., HNO_3 7½ lb., H_2SO_4 10 lb., AmOH 6 lb.

Wash Liquids and Special Fluid Reagents.

Those in the following list marked with an asterisk will invariably be required in rock analysis and should be made up before analytical work is commenced. They are conveniently stored together on one shelf in Winchesters. Other wash liquids given in this list are for special methods and need not be prepared until the necessity arises. Wherever water is used it will, of course, be distilled water. To prevent possible confusion it is advisable to label those marked with a † "Without potassium perchlorate" and "With potassium perchlorate" respectively.

* *Ammonium chloride.* *2½ per cent. solution in water.* This wash liquid is prone to turn acid on boiling. It is therefore desirable to add a few drops of indicator, followed by a few drops of weak ammonia solution, until an alkaline reaction is just reached. If, on prolonged boiling, the reaction to the indicator becomes acid, the liquid should be carefully neutralized with ammonia and a drop or two added in excess.

* *Ammonium nitrate.* *1 per cent. solution in water.* This should contain a little indicator as it is prone, like ammonium chloride above, to turn acid on boiling.

**Ammonium nitrate.* *50 per cent. solution in water.* 10 c.c. of this solution are used in the determination of phosphorus.

**Ammonia.* *2½ per cent. aqueous solution.* This should be freshly prepared when required.

**Ammonium oxalate.* *1 per cent. solution in water.*

**Wash Liquid No. 1 for Alkalis.*† Absolute alcohol saturated with perchloric acid.

**Wash Liquid No. 2 for Alkalis.*† Absolute alcohol saturated with percloric acid and potassium perchlorate. Some of the solid is kept at the bottom of the bottle to insure saturation with potassium perchlorate at all temperatures.

Mercurous nitrate. *2 per cent. solution in water.*

**Woy's Wash Liquid.* The ammonium phosphomolybdate preciptate is washed with liquid which is made up as follows: Dissolve 50 g. of ammonium nitrate in 1 litre of water and add 10 c.c. of concentrated nitric acid.

**Magnesia Mixture Special.* Both this and Woy's wash liquid are required in the determination of phosphorus. It is prepared as follows: Dissolve 50 g. of magnesium chloride ($MgCl_2.6H_2O$) and

100 g. of ammonium chloride in 500 c.c. of water. Add ammonia until the reaction to litmus is alkaline and allow to stand overnight. If any preciptate has formed it is filtered off. The solution is then made just acid with hydrochloric acid and diluted to one litre.

Calcium chloride. 10 *per cent. aqueous solution.* Together with zinc nitrate solution, this will be required in the determination of fluorine.

Zinc nitrate for fluorine. This is prepared as follows: 10 g. of zinc oxide are dissolved in a dilute solution of nitric acid consisting of 20 c.c. concentrated nitric acid and 180 c.c. of water.

Ammonium bichromate. This and the two following solutions will be required only if the chromate method for barium is employed (see p. 166). Barium will usually be determined as sulphate. 100 g., tested for freedom from sulphate, are dissolved in one litre of water.

Ammonium acetate. 300 g. are dissolved in one litre of water and the acid reaction is neutralized by the careful addition of ammonia.

Ammonium acetate wash-liquid. 20 c.c. of the last solution are diluted to one litre.

Nitric acid (sp. gr. 1·44). This will be used for the strontia determination and is made by admixture of ordinary nitric acid of sp. gr. 1·42 and fuming acid of sp. gr. 1·50, using a glass hydrometer.

Standard Solutions and their Preparation.

Potassium Permanganate $N/10$.

3·16 g.* of potassium permanganate are weighed out on a watch-glass, transferred by means of a jet from a wash-bottle into a 600 c.c. beaker, and dissolved in several hundred c.c. of water. The solution is filtered through glass wool, the filtrate being collected in a 1,000 c.c. flask. The volume is made up to a litre, the liquid well mixed and transferred to a glass-stoppered bottle which has been painted over with black enamel to exclude light. The liquid is then allowed to stand for several days, preferably a week, by which time it may be assumed to have reached a stable condition and is ready for standardization.

Standardization is effected by titration with sodium oxalate in the presence of sulphuric acid. Washington, in the fourth edition of his "Chemical Analysis of Rocks," recommended that, since the iron titrations are all carried out at laboratory temperature, the standardization of permanganate should also be carried out at that temperature instead of the more usual 60-70° C. This procedure, however, is extremely slow, each titration taking about fifteen minutes to carry out, and greater accuracy is claimed for the following method:

* If a considerable amount of analytical work is to be done, time will be saved by making up two litres.

2 g. of A.R. sodium oxalate are dried in an air oven at 130° C. for thirty to sixty minutes. Three portions of 0·25 g. of the salt are then weighed out accurately, and dissolved in 250 c.c. of cold dilute sulphuric acid contained in a 600 c.c. beaker. The acid solution is prepared by adding 5 c.c. of concentrated acid to 95 c.c. of freshly boiled and cooled water. To the liquid, which should have a temperature between 15° and 30° C., is rapidly added from a burette 90-95 per cent. of the volume of potassium permanganate calculated to be necessary. When decolorized, the liquid is warmed to 60° C., and titration completed drop by drop until the first pink tint appears. A blank is carried out and the volume needed to produce the same tint of colour in the solution is subtracted.

From the weight of sodium oxalate used in each case, the metallic iron equivalent of 1 c.c. of the permanganate is calculated. There should be good agreement between the results. If there is not, two or three more portions of sodium oxalate are weighed out and titrated, when three or four of the results should be in close agreement. Their mean is taken as the correct figure. From this the normality of the solution may be calculated (it will be somewhere near to $N/10$), as well as the FeO equivalent of 1 c.c. of the solution. It is this last figure which is written on the label and used in all the calculations of iron.

If stored in the dark, and the mouth of the bottle is kept clean, the solution will keep well, probably for a year or more. It is advisable, however, to re-standardize the solution every six months.

$N/50$ Potassium Permanganate.

50 c.c. of the $N/10$ permanganate are withdrawn with a pipette and run into a 250 c.c. measuring flask. The volume is then made up to the mark with distilled water, the whole thoroughly mixed, and stored in a black enamelled bottle in a dark cupboard. It does not keep quite so well as the $N/10$ permanganate, but more is easily prepared by dilution of the stronger solution.

Since this $N/50$ permanganate is used in the colorimetric

comparison for manganese, its MnO content is required. This is readily calculated from the normality figure of the approximately $N/10$ solution.

STANDARD TITANIA SOLUTION.

Several grams of pure recrystallized potassium titanofluoride K_2TiF_6 are spread on a clock-glass and dried in an air-oven at 150° C. for a couple of hours. At this temperature the salt is completely dehydrated and its titania equivalent will be approximately 33·3 per cent.; nevertheless the resulting solution will require to be standardized gravimetrically. A titania solution equivalent to 0·001 g. TiO_2 per c.c. is the most suitable strength, and accordingly 3.·00 g. are weighed out, accurate to a centigram.

Every trace of fluorine has to be expelled in the subsequent procedure, otherwise the colour yielded by the solution with hydrogen peroxide will be bleached according to the amount of fluorine and sulphuric acid present and, as a result, all the titania determinations will be high.

The salt is placed in a 4-inch platinum basin, 100 c.c. of 1 : 1 sulphuric acid are added, and the mixture is evaporated on the sand-bath (in a fume cupboard) until white fumes of SO_3 escape freely. The contents are maintained in this condition for half an hour and then allowed to cool. When sufficiently cool, the sides of the basin are washed down with a jet from the wash bottle and water added until the original volume is restored. The mixture is then evaporated to strong fuming again and the process carried out yet a third time.

When cool, 10 c.c. of 1 : 1 sulphuric acid are added (or sufficient to insure that sulphuric acid constitutes 5 per cent. by volume of the final solution). When quite cold, the liquid is diluted to one litre in a measuring flask.

In order to standardize the solution, two portions of 50 c.c. are taken, each diluted to 200 c.c., brought to the boil and the titanium precipitated as metatitanic acid with a slight excess (6 drops of 1 : 1 solution) of ammonia. Boil for two or three minutes before filtering, and wash the precipitate with hot water until the filtrate gives no re-

action with barium chloride solution. A little potassium sulphate may still remain occluded by the precipitate, but the error is of no consequence in ordinary work.* The precipitate is ignited moist and weighed as TiO_2. The content of TiO_2 per c.c. of the solution is calculated from the mean of the two results and the bottle labelled accordingly. If the agreement between the two determinations is not excellent, the procedure should be repeated with one or two more 50 c.c. portions and the mean of the most concordant results taken.

The stopper of the storage bottle should be vaselined and the liquid withdrawn by a pipette — never poured. The solution keeps well.

Some workers prefer to use the oxalate in preparing a standard solution of titania, arguing that, in the case of the oxalate, complete destruction is easier and its presence more readily ascertained (Washington, 4th Edn., p. 68). In this case, 4·42 g. of recrystallized and air-dried $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ are placed in a 500 c.c. Kjeldahl flask, and 8 g. of ammonium sulphate and 100 c.c. of sulphuric acid added. The liquid is gradually brought to the boil and boiled for 5-10 minutes. After cooling, it is poured into 700-800 c.c. of distilled water, further cooled and diluted to 1,000 c.c. This solution should contain 0·001 g. of TiO_2 per c.c., but the actual content should always be checked by precipitating with ammonia, or preferably cupferron, and igniting to TiO_2.

Standard Chromium Solution.

0·1276 g. of pure potassium chromate (K_2CrO_4, not bichromate) is weighed out accurately, dissolved in water rendered alkaline with a little sodium carbonate, and made up to 500 c.c. in a measuring flask. The solution will then contain 0·0001 g. of Cr_2O_3 per c.c., and is of suitable strength for the colorimetric comparison of chromium test solutions.

Standard Sodium Chloride Solution.

This will be used in the estimation of chlorine where the

* H lebrand-Lundell, p. 458.

chlorine content is small (less than 0·15 per cent.)—*i.e.*, in the majority of cases. A suitable strength is 0·1 g. NaCl in 100 c.c. of water, when 1 c.c. of the solution will contain approximately 0·0006 g. of chlorine.

Standard Copper Solution.

This will be required if the author's colorimetric method for copper (p. 143) is applied. The standard solution contains 0·00001 g. Cu per c.c. This is prepared by dissolving 0·3928 g. of A.R. copper sulphate ($CuSO_4.5H_2O$) in one litre of water to which a few drops of sulphuric acid have been added to prevent hydrolysis. When required for use, 25 c.c. are drawn off with a pipette and diluted to 250 c.c. in a measuring flask.

Standard Iron Solution.

The need for this will arise only very occasionally. Its use is confined to those cases where the amount of phosphorus present is in excess of the total iron and alumina, when, if iron is not added to balance matters, calcium will be precipitated with the iron and alumina as calcium phosphate (see pp. 56 & 212); and to the colorimetric comparison of manganese, when it is sometimes desirable to equalize the iron content of the comparison and test solutions (see p. 105).

A.R. ferric alum is weighed out accurately and dissolved in water to which a few drops of 1 : 1 sulphuric acid have been added. The strength of the solution to be used will depend on the particular requirements of each case.

CHAPTER III

SAMPLING AND CRUSHING

No matter how much care and painstaking effort are expended on the analysis, all will be wasted if the sampling and crushing of the material have not been properly carried out. Worse than this, others besides the original analyst may be deceived by the results. In this connection it is instructive to compare the figures obtained by different analysts on precisely similar material from the same quarry. With analysts of repute, the differences will be caused almost wholly by the efficiency or otherwise of the sampling, and will increase as the texture becomes coarser or more uneven.

With a fine-grained basalt or dolerite as little as 30-40 g., when crushed and powdered, will be quite representative; but unfortunately there are not many other rocks which fall into this class, only certain uniformly and closely-grained hornfelses, schists, spilites, fine tuffs, shales, slates, and other sediments.

When the rock contains megascopic phenocrysts or displays banding in the hand specimen, it is best to take about 80-100 g. and crush the whole of this amount. With more marked inequalities of chemical composition due to banding or porphyritic crystals, the only reliable procedure is to break an entire hand specimen into small lumps, and crush the whole until the largest lumps are less than ½ inch. The material is then tipped into a conical heap on a sheet of cartridge paper, smoothed out into a circle with a spatula, and carefully sampled by quartering. With coarsely porphyritic rocks several pounds of material should be broken up in this way, quartered, and re-quartered, about 100 g. being crushed for the analysis. Those unacquainted with methods of sampling will do well to look them up in any textbook of assaying for precious metals.

In the case of very coarse pegmatites, " giant " granites, and banded rocks in which the individual bands are several inches across, satisfactory sampling may be almost beyond the equipment of an ordinary laboratory. Up to ½ cwt. of material may need to be crushed in a ball-mill, but then there will inevitably be serious contamination with steel. Removal of this by magnetic methods unfortunately removes magnetite as well. A method suitable for some cases of coarsely banded and clotted rocks, such as thermally altered limestones, etc., is to make a very representative collection of chips in the field (amounting in the aggregate to several pounds) and then to have these coarsely crushed and repeatedly quartered in the laboratory, until a sample of suitable bulk is obtained.

Turning to the process of crushing, the first essential to be remembered is that all of the material, once placed in the mortar, must be crushed until it is of the requisite grade. When a sieve is used—and the author does not deprecate the use of a hard brass sieve for most work—the last part of the material tends to crush and pass through very slowly, so that there is a natural temptation to throw it away. Reflection, however, shows that this consists of the hardest and most resistant particles of the rock which are naturally concentrated in the sieve at this stage. To throw this material away, means that both samples and analysis are rendered unrepresentative of the rock. When the crushing is left to an assistant, this malpractice is particularly prone to occur.

The crusher used is a percussion mortar of hardened steel made in three parts—base, cylinder, and pestle—with a high cylinder into which the pestle fits snugly so as to prevent particles and dust from flying out. Ordinary diamond mortars may be used, but they are usually too small, the largest made being scarcely big enough for rapid crushing. Moreover, diamond mortars are provided with a small screw-on ring or collar in place of the cylinder; but the screw collar and pestle are apt to jam, causing loss of valuable time. The type of crusher used in the Geochemistry Laboratory of the Imperial College of Science and Technology is shown in Fig. 1. The top of the base and the lower

end of the pestle are specially hardened.

The rock is first broken upon a plate of hardened manganese steel into small pieces which can be dropped into the crusher. If much rock crushing has to be done in a laboratory it is convenient to have a crushing table made, as in Fig. 2. This consists of a specially sturdy and heavy stool with legs made of wood 3 inches square surmounted by a wooden top which is covered by an iron plate (½ inch thick). Asbestos wool is packed between the plate and wooden top to deaden the noise. A square wooden collar fits around

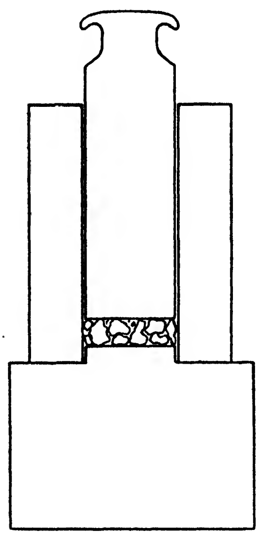


FIG. 1.—STEEL PERCUSSION MORTAR FOR ROCK CRUSHING.

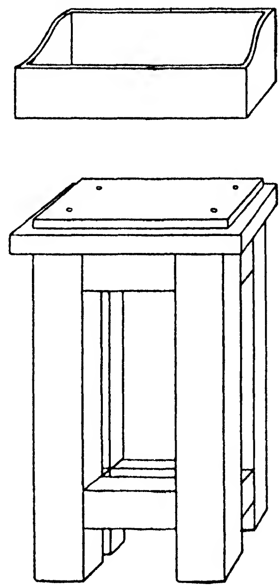


FIG. 2.—TABLE FOR BREAKING AND CRUSHING ROCKS.

the iron plate and stands up 6 inches above it, except on the side facing the worker, where it is only 2 inches high to allow for the hammer handle. The wooden collar prevents many pieces from flying about, and, being removable, it allows of the plate being properly dusted after use.

The specimen having been broken up in this way and sampled, several lumps of the material selected for analysis are placed in the crusher, the pestle put in position, and six

or eight heavy blows given with either a mallet or hammer. *A rotary motion of the pestle, causing grinding, should be avoided.* The material is then tipped into a 90-mesh sieve (a sharp tap or two on the base will dislodge any material inclined to stick or pack), and, after sieving, the coarse part is returned to the crusher *without loss*, which is a simple matter if a piece of folded paper is used. The process is repeated over and over again, additional material being added as required, but the crusher should not be kept more than one-third full. It will also be found that more than eight to ten strokes on the pestle between each sieving is a waste of physical energy. As already stated, *the crushing must be continued until the last residuum will go through the sieve.*

The type of hammer or mallet employed is a matter of importance. For most purposes a 1-lb. hammer will be too light. With rocks requiring a high crushing load, such as granitic and dioritic gneisses, and many members of the charnockite series, the most rapid crushing can be achieved by the use of a 4-lb. square-faced hammer as used by stonemasons and some geologists. However, there is then a decided risk that small particles of steel from the crusher may get into the pulverised sample. It is for this reason, too, that any rotary or grinding motion of the pestle must be avoided. All will depend on the hardness of the rock, the quality of the steel, and the amount of force employed. It is advisable, therefore, to test the pulverized sample for metallic iron before commencing an analysis (see p. 23) until the exact behaviour of a particular crusher in this respect is known.

If the use of a hammer is introducing iron into the sample, a heavy wooden mallet should be substituted. A suitable mallet consists of a cylindrical block 6 inches in diameter and 12-14 inches long, with a handle of about 16 inches. The block should be a specially selected piece of a very hard colonial wood which does not splinter at all easily, the handle being best made of oak or ash. About ½ inch back from each end of the mallet an iron ring is held on by three screws. The purpose of this is to prevent the end of the block crumpling up and disintegrating too rapidly. Such a mallet requires to be specially made, and is shown in Fig. 3. A

carpenter's mallet will not stand up to the strain for long. A mallet of the type described above is very satisfactory for a time, but, after considerable usage, the ends begin to break up and particles fly about during the crushing. A temporary cure may be effected by sawing an inch off each end of the block and putting the iron rings back accordingly. When using such a mallet, care must be taken to see that wood chips are not getting into the sample. If the sieve is too near the mallet, wood will almost certainly go in.

In short, an ideal method for crushing rocks and minerals for analysis has yet to be devised. The introduction of steel, in addition to disturbing the FeO figure, may increase the content of nickel and manganese. The introduction of wood will cause a short total, and will probably lead to reduction of ferrous iron to metal and consequent alloying

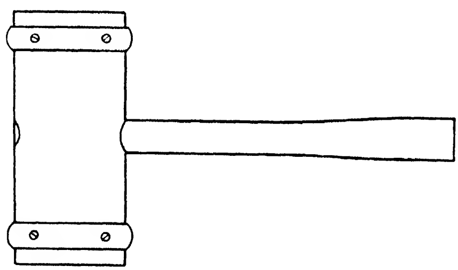


FIG. 3.—SPECIAL MALLET FOR ROCK CRUSHING.

with the platinum crucible during the main sodium carbonate fusion. This, if not detected and allowed for (see p. 225), will further reduce the summation. The ferrous iron determination will also be disturbed, some permanganate being used in oxidizing the organic matter. Nevertheless, the introduction of wood is not nearly so serious as contamination by iron. Wood can readily be floated off with water, but removal of iron is not practicable, for its complete removal cannot be effected magnetically without also removing magnetite and other magnetic minerals.

During crushing, the crusher may be supported on the iron plate of the special table described above. A large chopping block or tree trunk of suitable height is ideal, but may be difficult to procure. A narrower tree trunk,

6 inches or more in diameter, can be rendered very effective by having a band and leg supports of wrought iron fitted to it, as shown in Fig. 4.

The material which has passed through the 90-mesh sieve is thoroughly mixed and put into specimen tubes, care being taken to avoid draughts and undue loss of rock-dust in consequence. If flakes of mica are present, care should be taken to see that they are evenly distributed throughout the powdered sample. The material will not require grinding in an agate mortar except for the determination of alkalis, but in this case the grinding can be done in the agate mortar immediately after weighing out and before the process of mixing with ammonium chloride and calcium carbonate is commenced. Grinding may also be required in special cases when minerals refractory to a mixture of hydrofluoric and sulphuric acids are present in quantity—*e.g.*, garnet, staurolite, ilmenite, tourmaline. The task of grinding in an agate mortar is not a lengthy one after the material has been through a 90-mesh sieve.

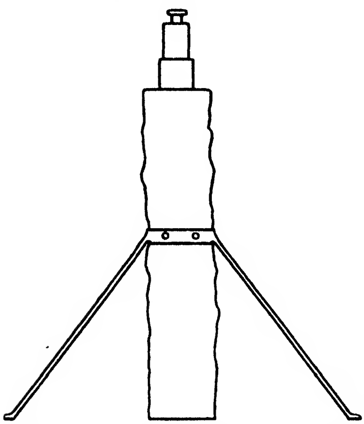


Fig. 4.—Use of Tree Trunk as Stand for Rock Crusher.

The use of a 90-mesh sieve, as described above, is extremely convenient; it affords the most rapid method of crushing, and for the most part the sample does not require further grinding. Some authorities, however, consider that the use of a sieve is to be deprecated. Certainly the sieve should be of brass and not copper, and it should be scrutinized each time it is used, but in the author's experience such a sieve is satisfactory for all ordinary work. Once a sieve shows signs of verdigris it must be discarded. The contamination produced by a good brass sieve is not nearly so serious as may be supposed. Using the sensitive method for copper described on p. 143, no difference of any importance

could be found on two portions of the same material one of which had been crushed with the aid of a brass sieve and the other without. In the author's opinion, therefore, the use of a sieve is only inadmissible when minute amounts of copper, zinc, tin, or lead are being sought (the tin and lead will be present in the tinplate and solder of the sieve and its receiver). In such cases the place of a brass sieve is conveniently taken by 100-mesh silk bolting cloth.

If no sieve is used, the material is crushed as far as practicable in the crusher and then ground in small amounts at a time in the agate mortar. The labour involved is much greater than in the method described above, and at least one hour's grinding will be required after the crushing. Contamination by silica from the agate pestle and mortar then occurs on a small scale, but, since silica is usually the principal constituent, this is relatively unimportant.

Inspection of Powdered Sample before Commencing Analysis.

The final powdered sample, whether crushed by the analyst himself or otherwise, should be tested for iron. This simple test is carried out in two or three minutes as follows: A gram or so of the powder is placed in a test-tube and dilute hydrochloric acid added. A characteristic odour is given to the escaping hydrogen if iron is present, even in very small amount. If the operator is not accustomed to this smell, he cannot do better than carry out the same test with some iron scraps or filings. Effervescence observed may not be due to iron but to the attack of carbonates or merely escaping air bubbles.

Wood, cotton-wool, hair, or fibre can be tested for, and removed if necessary, by pouring the powder into a beaker of water when these substances will float.

When a mineral has been separated from a crushed rock by means of one or other of the heavy liquids used for the purpose, special care must be taken to insure that the mineral grains are washed free from the particular liquid. If bromoform or methylene iodine has been used, the organic matter left in may well be sufficient to cause reduction of

ferrous iron to the metal and consequent alloying with the crucible during fusion with sodium carbonate. An attempt may have been made to wash these liquids out by means of benzene or alcohol, but these last must be completely removed by spreading the powder in a thin layer in an air oven at 110° C. (after thorough drying in air) before the analysis is commenced, or reduction of ferrous iron to the metal may equally well occur during the main fusion.

Thoulet's solution (K_2HgI_4) is best removed by washing, first with a hot solution of potassium iodide, and afterwards by repeated washing with hot water until the washings give no red precipitate with dilute copper sulphate solution. If the potassium mercuric iodide is not so removed, the platinum crucible may be damaged, in addition to obtaining a short summation. Clerici solution is another heavy liquid often used for the final purification in mineral separations. It consists of a more or less saturated solution of thallous formate and thallous malonate, either in equimolecular proportion or equal weights. If this is not thoroughly washed away in hot water, similar troubles will be experienced. In the sodium carbonate fusion, the organic matter reduces thallium to the metal which promptly alloys with the platinum crucible causing serious damage. A simple test for thallium is the green colour imparted to the bunsen flame when a few mineral grains are introduced on a platinum wire. Such tests and washings can be very rapidly carried out, and valuable time and material may be wasted if they are omitted.

Under some circumstances, as for instance when very small amounts of iron have to be determined (quartz, glass sands, felspars, alaskites, etc.), or where the $FeO:Fe_2O_3$ ratio is of special importance, it may be desirable to ascertain the actual amount of metallic iron present and to correct for it. In this connection Dr. M. H. Hey has suggested that this information might be obtained by either of two methods :—

(*a*) Digestion with mercuric chloride solution ;

(*b*) Heating in a current of dry chlorine at 250-300° C.

The chlorine method removes not only metallic iron, but decomposes and removes both FeS and FeS_2. Provided

the chlorine contains no hydrochloric acid, it does not attack most rock-forming minerals, so that this method could be used to determine metallic iron and iron in sulphides. In this connection the method has not been fully tried out (*Mineralog. Mag.*, 1932, **23**, 48-50), though its application to the determination of sulphur in sulphide is described on p. 207.

Contamination of Silicate Samples Crushed in Steel Mortars.

In silicate analysis the steel introduced during crushing in a percussion mortar is a factor that ought to be considered. In the past it has been generally assumed that the amount of contamination is small, if the crushing is carried out solely by percussion with avoidance of a grinding motion, or that in any event the error is not easily avoided.

It will of course be obvious that the use of a stainless steel with say 18 per cent. chromium and 8 per cent. nickel will be highly undesirable and this is the more so in that chromium and nickel are usually present in minute amounts in rocks. Yet the use of a decidedly manganiferous steel may be justified not only on account of its extreme toughness and resistance to wear generally, but on account of the fact that most rocks already contain several tenths of one per cent. of MnO and that therefore a minute addition to this figure will be of no significance. Whatever the steel employed, it should have as low as possible a content of those elements usually present in only minute amounts in rocks, *e.g.*, chromium, nickel, vanadium, molybdenum, tungsten, copper, cobalt. The presence even of columbium and tantalum in a steel mortar have been reported* ; indeed any of the usual ferro-alloy elements may be encountered in quantity.

Far and away the greatest contaminant will be iron. Here it might be argued that, apart from a few things like high-grade glass sands and ceramic felspars, there is already so much iron in the sample that a small addition would be without significance. But it has to be borne in mind that

* H. Rankama. Bull.comm.géol.Finlande, No. 133, 11 (1944).

although the amount of iron introduced may not significantly affect the figure for the total iron content, it will appreciably raise the value for ferrous iron and therewith lower the value for ferric iron (the latter partly compensated), since 0.03 per cent. metallic iron corresponds to almost 0.1 per cent. ferrous iron.

Little published information exists on this question, but a useful contribution has recently been made by E. B. Sandell* who has experimented with the crushing of quartz and microcline in a Plattner type mortar (variety or composition of steel not stated). His results (given below) with this type of mortar show considerably greater contamination when the collar is used than when it is not used.

Amounts of Metals Introduced in Crushing Quartz and Felspar in Steel Mortar

Sample	Fe	Mn	Cr	V	Ni	Co	Cu
				P.p.m.			
Clear quartz crystal	280	1·8	0·4	<0·1	0·25	<0·1	0·35
Do. (without collar)	190						
Milky Vein Quartz (with collar)	220						
Microcline (with collar)	170						
Microcline (without collar)	55						

As we might expect, the degree of contamination here is much greater for a presumably unstrained quartz crystal of hardness 7 and devoid of cleavage than it is for a cleavable mineral like microcline with hardness 6. We might expect contamination therefore to be greatest in the crushing of rocks with the greatest proportion of free quartz. Rocks with much topaz (H.8), such as greisens, or with much corundum (H.9), as in corundum syenites, may be expected to give rise to maximum contamination.

Assuming the clear quartz crystal he used to be chemically pure, an assumption that would nevertheless have been better checked as regards iron, Sandell concluded that the amount of iron introduced — 0.02 to 0.03 per cent. Fe — would not significantly affect the figure for the total iron content though it would appreciably raise the value for ferrous iron. He further concluded that, if these experi-

* Ind. Eng. Chem., Analytical Edn., 1947, 19, (9), 652-653.

ments could be considered representative, the amounts of trace constituents contributed by the Plattner mortar were small enough to neglect, though the chromium content of the mortar used might be somewhat higher than desirable when acid rocks were involved.

For a discussion on sampling, the reader is referred to F. F. Grout's paper " Rock Sampling for Chemical Analysis," *Am. J. Sc.*, 1932, 5th ser., **24**, 394-404.

CHAPTER IV

A. CONSTITUENTS TO BE DETERMINED IN ROCK ANALYSIS

In rock analysis it may be taken for granted that the following *thirteen constituents* will all be present and require determination : SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, $H_2O+110°$ C., $H_2O-110°$ C., P_2O_5. Indeed, this number is the minimum that must be determined if it is wished to calculate the norm of the rock.

In many rocks, particularly those which are somewhat decomposed, carbon dioxide is present in appreciable amount. Carbon dioxide, however, is not always a measure of the freshness of a rock, for no reasonable doubt now remains as to the primary nature of the calcite to be found in nepheline-syenites, alnoites, and associated rocks, and sometimes in granites (*cf.* Washington, p. 17). Cancrinite (see p. 274) is believed to be primary in numerous instances. Moreover, the carbon dioxide of scapolitized rocks is not due to weathering. The non-determination of carbon dioxide in such cases will lead to (*a*) shortage in the summation ; (*b*) lime, which should be assigned to calcite, will be calculated as normative diopside. The figure for the latter will be too high, and corresponding amounts of alumina and silica will be used when they should have been assigned to normative corundum, silicate, or quartz, respectively. If *carbon dioxide* is appreciable, its presence in a rock will be indicated by a thin section under the microscope, but there is a much more sensitive test which in three minutes will reveal as little as 0.05 per cent. carbon dioxide (see p. 237).

After carbon dioxide, which may be absent or less than 0·1 per cent. in many rocks, as a rule *sulphur* is the next in importance. Here again the microscope will show whether

this should be determined and also its mode of combination. Pyrite is the most common constituent carrying sulphur, and in this case the non-determination of sulphur will not affect the ferrous iron of the analysis. It will be the total iron and so the Fe_2O_3 figure which will be too high when it comes to calculation of the norm.* Sulphur is a most ubiquitous constituent and in mineralized rocks it may be considerable, giving rise to difficulties in the analysis (see p. 204). Consideration should also be given as to whether only acid-soluble sulphur, or total sulphur by the fusion method, or both methods will be required.

If there is still a shortage after these constituents and barium have been determined, in most cases it strongly suggests the presence of appreciable *fluorine.* If the microscope reveals topaz, tourmaline, fluor, chondrodite, etc., the necessity for a fluorine determination is obvious. The fact must not be overlooked, however, that in a number of minerals OH groups may be replaced by fluorine. Except in phlogopite, fluor, topaz, etc., where the fluorine is certain to be high, the content of this constituent cannot be gauged by the amount of the mineral present. In the author's experience a fluorine determination is called for whenever a rock is at all rich in mica or amphibole. These are very strong reasons for deprecating the suggestion of Washington (p. 7) that fluorine may be calculated from micrometric determinations of apatite. It should be borne in mind that the oxygen equivalent of fluorine is almost exactly one half, so that a total of 97.5 in the analysis of, say, a phlogopite may indicate the presence of about 5 per cent. of fluorine. It is evident from this that a fluorine content of less then 0.25 per cent. is not likely to be suspected solely on account of a deficiency in the summation.

One or both of the elements *barium and strontium* frequently occur amongst all petrographic types, igneous, metamorphic, and sedimentary, so that they should always be sought in an analysis having any claim to completeness. The information so obtained is of more than passing interest ; indeed, in some recent petrological enquiries it has been of

* It is not usual to return sulphur as FeS_2 in the analysis. Neither should it be returned as SO_3, unless sodalite is present.

special importance. An appeal has been made by Prof. A. Holmes for more frequent determination of barium and strontium in chemical analyses of rocks (sedimentary and metamorphic, as well as igneous), and particularly in analyses of rock-forming minerals, so that it may become possible to establish exactly in what crystalline phases barium and strontium are concentrated.* If the rock comes from one of the well-known barium and strontium regions of the world (see p. 285), it certainly behoves the analyst to seek these constituents, as they may be present in quite appreciable amount (up to about 0.25 per cent. each).† If baryta and strontia are omitted, the baryta, in the absence of sulphate, will probably not be caught anywhere in the analysis, but nearly all the strontia will be reckoned as lime. The necessity for weighing out separate portions does not arise, as strontia is determined in the ignited CaO preciptate, and a residue in the manganese separation is used for baryta. If barium and strontium are to be determined, unless the fact be decided before commencement of the analysis, time will be wasted. Baryta is usually present in greater amount than strontia and is the more readily determined, so that, if a choice has to be made between the two, it will be better to separate baryta.

Chlorine is present in the majority of rocks to the extent of only a few hundredths of one per cent. but, in alkaline types and rocks which have been scapolitized, its determination may become essential. If sodalite or ameletite be suspected, a chlorine determination will settle the point. Specimens collected from the seashore may be impregnated with salt, which, however, can readily be leached by water from the powdered material and separately determined, the chlorine found by this method being calculated as NaCl and the figure for Na_2O suitably adjusted.

Unless gypsum, haüyne, or nosean (noselite) are present, it is unlikely that *acid-soluble sulphate* will be found. Since the test occupies only a few minutes, it is as well to apply it to all alkaline volcanic rocks on the off-chance that haüyne or nosean have been missed in thin section. It

* A Holmes and H. F. Harwood, *Q.J.G.S.*, **88**, 424 (1932).

† A highly felspathic granulite from Ceylon gave 0·72 per cent. BaO.

should be borne in mind that some scapolites contain an appreciable amount of SO_3.

The determinations of *chromium and vanadium* are usually carried out together, since although the operation is a long one, once chromium has been dealt with, vanadium takes only a further half hour or so. Vanadium will almost invariably be found in any rock, igneous, metamorphic, or sedimentary, but the same cannot be said of chromium, though it is commonly present. The two constituents vary independently of one another. As a rule the content of chromium in igneous rocks is small in the acid and intermediate divisions but rises rapidly towards the basic and ultra-basic types. Its determination in the case of dunites and peridotites containing possible chromite, as well as in rocks having a chromium-bearing mica (fuchsite), chrome-diopside, chrome-tremolite, uvarovite (the chromium-bearing garnet), or tawmawite (chrome-epidote) is clearly essential. In most rocks with the basicity of basalts chromium will be appreciable — though it is less in the alkali-basalts.

Vanadium in igneous rocks is contained principally in the ferromagnesian minerals — *e.g.*, biotite, amphibole, and pyroxene; thus its content will vary according to the development of these minerals. The determination of vanadium and chromium is especially called for in the analysis of these minerals, as well as in pyroxenites and amphibolites.

In sediments, vanadium is sometimes concentrated in iron ores, manganese ores, and coals, as well as in laterites and bauxites. Clays from regions of arid climate are more likely to contain vanadium than others.

There is no risk of chromium escaping precipitation by ammonia. Vanadium is also completely precipitated by ammonia in the presence of the ferric salts invariably present at this stage of the analysis. In extreme cases neglect of vanadium introduces error into both the iron determinations (see p. 89). Against the smallness of the chromium content of most rocks is the mitigating circumstance that chromium can be determined with the greatest accuracy, correct to three places of decimals of one per cent. With such an accuracy quite small amounts of chromium may have a

geochemical significance — *e.g.*, it is clearly worth while demonstrating that one series of rocks contains, say, 0.002-0.007 per cent. Cr_2O_3 when in another the figure varies perhaps between 0.030-0.040 per cent. Cr_2O_3.

Of the remaining constituents, *nickel* is generally of more significance than zirconia. It occurs, usually in a few hundredths of one per cent., in many basic rocks where it is present in the ferromagnesian minerals, particularly amphiboles, olivine, and serpentine. In ultrabasic rocks and meteorites the nickel content is usually much higher. If, then, the rock is fairly basic, nickel should be sought, and especially if there is much olivine and serpentine, or if pyrrhotite is present. Nickel can be determined with great accuracy (see pp. 139 & 186). If omitted, most of the nickel runs through the analysis, though a little (often about one-third) is precipitated with the R_2O_3.

If zircon is present in sufficient amount to be noticeable in thin section under the microscope, it is as well to determine *zirconia.* Zirconia rarely rises to appreciable amount except in some alkaline rocks, particularly the nepheline-syenites. Richness in zirconia will then be obvious under the microscope and, in addition to zircon, eudialyte may be present. The non-determination of zirconia leaves an error in the alumina, but in the great majority of cases this will be either very slight or neglible. The fact that zircon may be abundant in the non-magnetic concentrate of the heavy residue does not necessarily mean that zirconia is present in quite appreciable amount in that particular rock. The enormous degree of concentration which has been effected must not be overlooked ; indeed, 0.01 per cent. ZrO_2 in a rock may, in these circumstances, yield plenty of zircon. The same remark applies to several other minerals — *e.g.*, cassiterite, monazite, allanite, etc. Zirconia should never be calculated from micrometric determinations of zircon as suggested by Washington (4th Edition, p. 7).

The determination of *lithia* will rarely be necessary except in rocks suspected of containing lithia-mica. Nevertheless, lithia is a very common constituent in rocks to the extent of a trace, as is revealed by the spectroscope. The separation of lithia is a rather lengthy process and will in most

cases prove a waste of time unless there are good grounds for suspecting the presence of an appreciable amount. In practice, it is usual to examine the concentrated alkali chlorides, or the washings from the potassium perchlorate (see p. 86) obtained in the separation of alkalis, with a pocket spectroscope. Since this can be done in little time it is a pity that it should be neglected, as is so often the case. The observation of whether lithia is present as a " marked trace," " trace," or " absent," as revealed by a pocket spectroscope and platinum wire held in a flame,* affords comparative data which are well worth recording and not without geochemical and petrological significance.

Boron is another constituent which is rarely present in appreciable quantity. This is fortunate for two reasons :

(*a*) The determination is a lengthy one requiring special apparatus.

(*b*) The presence of much boron upsets the ordinary analytical procedures.

The presence of appreciable boron will be reflected in the occurence of boro-silicates such as tourmaline, axinite, datolite, dumortierite, etc., which, if not evident in the hand specimen, will have been discovered during the microscopical examination. The beginner will do well to avoid attempting the analysis of such rocks, leaving them until he has become proficient in the ordinary methods and can obtain help from an expert.

Copper is a constituent which, in the past, has rarely been determined in analyses of rocks, yet the researches of Sandberger and others have shown it to be very widespread in its occurrence. The reason for its non-determination was that the gravimetric method of separation as sulphide requires a very large sample (20-50 g.) if the copper is very low, as is usually the case. A highly sensitive colorimetric method using an organic reagent has been adapted to rock analysis by the author (p. 143) and by its means a CuO content of a few thousandths of one per cent. up to 0.25 per cent. can be determined with considerable accuracy on a

* The use of an electric arc and a better class of spectroscope is an arrangement which is too sensitive and will show lithia in nearly every rock.

sample of only 1-2 g. This range covers the great majority of cases, and the analyst has no longer an excuse for the non-determination of copper. So far as results obtained by this method are available, copper appears to be more prevalent in the basic types, but not a rock has been examined from which it is absent. If the determination of copper is omitted, most of it escapes the analysis.

With regard to *beryllia*, it is probably true to say that the number of rock analyses in which this constituent has been determined may be counted on one's fingers. There is no doubt that the analytical problem has been mainly responsible for this state of affairs. As a result, our knowledge of the occurrence of beryllium was in an equally unsatisfactory state until the survey by Goldschmidt and Peters using physical methods (see p. 288). Its determination will be essential if beryl is present. Beyond this, little more can be said at the present juncture, but it seems clear that beryllia, in small quantity at least, must frequently be present in rocks. Its non-determination means that it will be reckoned with the alumina.

The *rare-earths* will be determined only when, as in some acid rocks, allanite or xenotime are developed, or the content of soda is very high, as in nepheline-syenites. They are particularly prone to occur in the pegmatites associated with nepheline-syenites. Non-determination of the rare-earths means that they will be reckoned with the alumina.

The determination of *carbon* will rarely be necessary in the analysis of igneous rocks, though graphite has been recorded from pegmatites, some dyke rocks, iron-bearing basalts, and syenites. In metamorphic rocks, particularly altered limestones, it is liable to occur as graphite, but it is in sedimentary rocks where carbon will be most frequently found. When carbon is appreciable, it usually imparts a dark colour to the rock, but such a colour may equally well be due to manganese. Shales are especially prone to be carbonaceous. When carbon is present as a hydrocarbon, analytical difficulties are introduced. Carbon manifests itself when the rock powder is decomposed with hydrofluoric and sulphuric acids, but it should be borne in mind that powdered pyrite does the same. Its non-determination

will mean a shortage in the summation.

Rubidium and cæsium, so far as rock-forming minerals are concerned, occur in appreciable quantities only in lepidolite. Unless this mineral is present in quantity, these constituents need not usually be considered. Lepidolite may contain from traces up to 3.73 per cent. of Rb_2O and from traces to 0.72 per cent. Cs_2O. These constituents may be detected spectroscopically but their determination is seldom carried out except in analyses of lepidolite. Pollucite, which contains 42.5 per cent. Cs_2O, and cæsium-bearing beryl are comparatively rare, but are sometimes found in cavities in granites. For rubidium in microcline, see pp. 293-294.

Molybdenum is rarely present in determinable amount even when a 5 g. sample is used, but just occasionally molybdenite occurs as an accessory mineral in granites when its determination may be worth while. *Arsenic* is another constituent which is rarely sought, though if present in an appreciable amount it will be detected along with molybdenum in the course of the method for chromium and vanadium. *Zinc* is not usually sought, though it has been found in granites and basic rocks. It is usually present in only minute amounts.

To sum up, the thirteen constituents mentioned at the beginning of the chapter should be the minimum in all cases of rock analysis. Carbon dioxide, baryta, strontia, and sulphur should also be determined in the majority of cases, and fluorine will be scarcely less essential. The test for lithia with a pocket spectroscope should not be omitted even if only thirteen other constituents are determined. Chlorine should not be omitted when alkaline volcanic rocks are being dealt with or when scapolitization is known to occur in the district. Next in importance come zirconia, nickel, chromium, vanadium, and copper, which should always be determined when questions of petrogenesis are involved. Acid-soluble sulphate (SO_3) is usually unimportant. Other constituents, such as lithia (gravimetric determination), boron, beryllia, rare-earths, molybdenum, and arsenic, will be determined only in special cases. If barium is appreciable it is as well to ascertain how much sulphur is combined with it in barytes (see p. 118).

B. DETERMINATION OF DENSITY OF SAMPLE.

It is usually desirable in scientific work that the chemical analysis of a rock be accompanied by a determination of the density, a task which often falls to the analyst. For this purpose the ordinary Walker steelyard is generally used (see Holmes's *Petrographic Methods and Calculations*, p. 32).

In the case of analyses of minerals for scientific purposes it is much more important that a density determination be made in order to allow the mineralogist to convert the analysis into terms of unit cell content. Here it is particularly important that the density be determined as accurately as possible on a portion of the actual sample to be analysed. The only allowable exception to this rule is where the mineral is so porous or colloidal, as some clays, that an accurate determination of density is not obtainable by any method. If the pyknometer is used and the sample is in the form of grains or has already been coarsely ground, it is important to see that all air bubbles are removed when the mineral is covered by the liquid. This is best done by using carbon tetrachloride instead of water and leaving the pyknometer in a vacuum desiccator overnight before weighing.

It may be added that the pyknometer method for densities of minerals is inferior in accuracy to the suspension method (as distinct from the method of hydrostatic weighing) unless the amount of material available is enough to half-fill the pyknometer with solid. The suspension method is probably preferable for all homogenous materials of densities below 4·1, provided the observer has sufficient patience in adjusting the specific gravities of solid and liquid, the density of the liquid is determined with a good pyknometer, and the temperatures are measured with adequate accuracy. In the pyknometer method water is a very poor displacement liquid, owing to its high surface tension; toluene is bad owing to a high co-efficient of expansion; carbon tetrachloride is generally the best liquid to use. For a discussion on the accuracy of specific gravity determinations, see F. A. Bannister and M. H. Hey, *Mineralog. Mag.*, **25**, 1938, pp. 30-34.

C. LIMITS OF ERROR

The limits allowed for the summation of a good rock analysis are 99·75 to 100·50. The lower limit of 99.50, given by Washington, is not satisfactory, for a consideration of the errors arising during analytical work — excluding losses due to sheer carelessness — reveals that they are nearly all additive. Dust falls into precipitates and solutions however carefully one tries to keep them covered, the washing away of reagents — particularly sodium salts — may not be quite complete, the reagents used may introduce in small amount some of the constituent sought, and finally the hygroscopic nature of some ignited precipitates are all factors making for a high summation. Provided all the constituents present have been determined, the author considers a total slightly in excess of 100 to be preferable to one short of this figure.

Totals below 99.75, provided there has been no loss of material, at once suggest that there are one or more constituents present in appreciable amount which have not been determined. Totals in excess of 100.5 suggest incomplete washing and ignition of precipitates.

In the analysis of most silicate minerals the same limits of error should apply. For analyses of other minerals, meteorites, etc., the limits may be extended slightly, according to circumstances. For location of errors, see Chapter IX.

CHAPTER V

COMMON OPERATIONS

WEIGHING.—The first requirement is to know the sensitivity of the balance to be used. Most sensitive balances are not intended to carry a load of more than 50 g. in each pan, and in practice it will probably be found that most of the crucibles and small dishes to be weighed are round about 20-30 g. If, therefore, the sensitivity is determined for a load of 25 g. in each pan, the figure obtained will probably be a fair average.

25 g. then are placed in each pan and the balance is allowed — by sleight of hand in releasing the handle — to swing about five small scale divisions to either side of zero. A magnifying lens (conveniently held in a copper-wire support stuck into a large cork) is so mounted that the pointer and scale divisions are magnified sufficiently to allow one to estimate to about one-tenth of a scale division. This lens will always be a great asset in weighing. The first two or three swings are ignored and then the end or turning-point of each swing is observed and quickly noted down, a visual estimate being made to a tenth of a scale division. Readings are taken from the centre, those to the left are counted as negative, those to the right positive, the observations being written down in the following manner :

	Left.	*Right.*
	+0·0	+3·6
	+0·1	+3·5
	+0·2	+3·4
	+0·3	
	0·6	10·5
Mean	0·15	3·5

Difference 3·35. Position of rest $\frac{0{\cdot}15+3{\cdot}5}{2}=+1{\cdot}8$ approx.—*i.e.*, 1·8 scale divisions to the right of zero.

There must always be one more reading on one side than the other. The variations in the swings should be regular; if not, there is either a disturbing factor such as draughts, dirt on the agate planes, or the knife edges may have been damaged, in which case the instrument will have to be reconditioned by the makers.

Assuming regularity of the swings, a number of observations — usually three or four — is made on either side. These are totalled and the mean taken. The difference between these two figures clearly represents the mean traverse of the pointer during these swings, so that the position of rest or zero of the instrument is given by half this number added to the mean of the left-hand turning points (the appropriate sign being observed). If the turning point is more than one scale unit out, as in the example given, it is corrected to within one unit by means of the adjusting screws on the balance arms or by the flag over the centre of the beam, whichever arrangement is provided. In this case the position of rest will need to be re-determined.

The position of rest having been ascertained with a 25 g. load, the sensitivity is then determined by adding 1 mg. to one side by means of the rider and re-determining the position of rest. Suppose that in the first instance the position of rest was $-0{\cdot}4$ and in the second case $-2{\cdot}8$, then the addition of 1 mg. has displaced the position of rest by 2·4 scale divisions and the sensitivity is expressed as 24. It is very convenient to have the balance adjusted to a sensitivity of 25 for reasons given below. The adjustment can be made by trial and error, using the gravity bob.

In the most accurate work the sensitivity method of weighing is adopted, but for all practical purposes, except when semi-micro methods are in use, a combination of the sensitivity method and the method of equal swings is employed. Thus, if the balance is adjusted to a sensitivity of 25 and the zero error is negligible, 0·2 mg. will displace the position of rest by 0·5 of a scale division. This, however, will mean that if the pointer swings x scale divisions on one side, it will go $x+1$ or $x-1$ divisions on the other side. Making use of this fact, the correct position of the rider can be found more rapidly than by trial and error.

The pointer is watched and the inequality of the swings noted. Thus 3 divisions in excess to the left will mean that the rider has to be placed 0·6 mg. further to the left (the rider beam should preferably be divided from zero over the left-hand stirrup to 10 over the right-hand stirrup, for use with a 5 mg. rider). It is advisable always to place the rider on the position indicated by these approximations and so test their accuracy, for there may be an error of one or two tenths of a mg. or the object being weighed may be hygroscopic and gaining weight. These advantages are well worth the little trouble of adjusting the sensitivity in the first place. Balances are often delivered adjusted to this sensitivity by the makers.

A precaution to be adopted at the commencement of each day's work, or whenever any rock powder has been spilt, necessitating cleaning of the balance pan, is to check the unloaded position of rest in the manner just described and if necessary bring it back to within one division of zero. This can be done in two or three minutes and is necessary for whichever method of weighing is adopted. The sensitivity will also require checking at intervals if the balance is being used continuously. Except in particularly moist conditions, as in certain tropical climates, the use of a desiccating agent in the balance case is probably unnecessary.

A good quality set of weights is required; these should be checked against one another at the outset and at intervals of several months if they are used very much. They should always be re-checked if a spot appears on them. Direct weighing of portions into a weighed dish or crucible is usually to be preferred to the use of a weighing bottle.

Filtration.—Skill in filtration is quite an important factor, for not only the speed but also the accuracy of the work may depend on it. If the filtration is proceeding very slowly, by reason of a poor funnel and badly fitting paper, it is unlikely that the precipitate will get its full quota of washings. Funnels vary considerably according to the accuracy of their angle of slope, etc., and it is a good plan to test the relative speed of the funnels at the outset and mark the best ones for general use. The filter paper should be

made to fit snugly into the funnel, particularly at the upper margin of the paper. The latter should not overlap the funnel, but should come somewhere between 5 and 15 mm. from the funnel edge. Different grades of paper will be required according to the nature of the precipitate. In general, a fast filter paper is used with a gelatinous precipitate, but a fine-grained crystalline precipitate will require a slow paper. The grade and size will generally be specified in the directions in this book. The filter paper should not be more than one-third to one-half full of precipitate.

The rate of filtration of an ordinary funnel can be increased by coating the inside with paraffin-wax, cutting ten to twelve lines extending about two-thirds of the distance from the apex to the rim, and then etching to a moderate depth with hydrofluoric acid.* A further improvement on these lines is embodied in the new Jena analytical funnel, which, in addition to being shaped at exactly 60°, is specially grooved to allow of exceptionally fast filtration. One of these funnels will save an appreciable amount of time in the filtration of the ammonia (R_2O_3) precipitate.

WASHING OF PRECIPITATES.—The wash solution will generally contain a salt with an ion common to the precipitate, usually an ammonium salt which gives no trouble in its volatilization on ignition. Thus the calcium oxalate precipitate is washed with a very dilute solution of ammonium oxalate, in which it is less soluble than in distilled water. In the treatment of a gelatinous precipitate which tends to go into colloidal suspension when most of the impurities have been removed, as in the case of the ammonia precipitate, the washing solution must contain an electrolyte which can be volatilized on ignition.

Insufficient washing will give rise to inaccuracy which may well be considerable; on the other hand, excessive washing will tend to dissolve some of the precipitate. The latter error, however, is much less likely to be so serious as the former. Indeed, in the author's experience beginners are particularly prone to insufficient washing and prefer to assume that the washing is complete rather than ascertain

* Hillebrand-Lundell, "*Applied Inorganic Analysis*," 1929, p. 89.

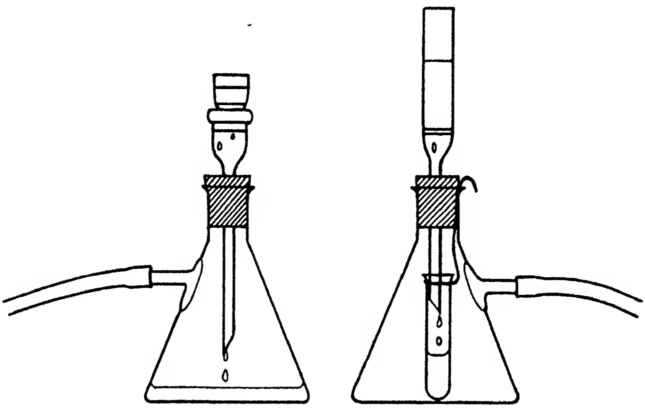
the fact by a simple test. With such methods they will never know where they actually stand with regard to impurities, and the standard of their work will in consequence be most erratic. The need for applying a test to the filtrate as it leaves the funnel to ascertain whether all the impurity is removed cannot be too strongly impressed upon the beginner, *but he must equally well note this word of warning : if the filtrate is to be used for another constituent, do not apply the test until it is obvious that the greater part of of the impurity has been washed away.* In this way he will soon learn the correct number of washings to be applied in every case, but even when he has done so he should still continue to test his filtrates. After experience, one such test may then indicate whether one or two more washings are required.

The jet from the wash-bottle is commenced gently and turned on to the clean upper part of the paper so that possible loss of precipitate by ejection is avoided. The jet is then lowered, working the precipitate down into the bottom of the paper, which should be not more than one-half filled with liquid. The liquid is then allowed to filter and drain. The most rapid washing is achieved in this way, using small quantities of liquid and allowing them to filter completely before the next portion is added. A further advantage, which may save as much or more time than that saved on the actual filtration, is the small volume of filtrate obtained. Care in this matter may obviate the necessity for reducing the volume of a filtrate by evaporation.

Suction Filtration.—When the precipitate is not to be ignited but merely dried before weighing, or the use of nitric acid renders paper unsuitable, filtration is carried out by means of a sintered-glass filter crucible or a Munroe crucible (see p. 5), for both of which suction is required. This is obtained by means of a glass filter-pump wired on to a water tap and connected to a thick-walled filtering flask as shown in Fig. 5. With this arrangement very rapid filtrations can be carried out, and, after use, the filter is cleaned by means of a suitable solvent. In the case of a Munroe crucible used for potassium perchlorate, provided it is always kept in an efficient desiccator, the perchlorate

need not be removed after weighing, thus saving one weighing for each potash determination. This is not altogether advisable when a sintered-glass filter is used, as it is more prone to variation in weight than a platinum vessel on account of surface absorption of moisture. Sintered-glass filters are best cleaned by drawing aqua regia through them, followed by a thorough washing with hot water.

Some filtrations which have to be done through paper are particularly slow — *e.g.*, the precipitate of mercurous salts in the determination of chromium and vanadium, the first precipitate of nickel glyoxime, etc., in the determination of nickel. In such cases an ordinary glass funnel is



(a) (b)

FIG. 5.—SUCTION FILTRATION.

(a) Ordinary, (b) special arrangement for determination of strontia.

fitted into the filter flask (Fig. 5), a small circle of specially toughened paper being folded and inserted as a protection to the tip of the filter paper, which is always its weakest point. The filter paper is then carefully placed in the funnel and well pressed down. The degree of suction which such an arrangement will stand can be learned only by experience. No. 54 Whatman filter papers are sufficiently tough to withstand suction filtration without the use of a toughened tip, but they are not suitable for very fine precipitates.

IGNITION OF PRECIPITATES.—The drying of precipitates before ignition is sometimes recommended, the method

usually adopted being to cover the funnel with a stretched wet filter paper, and to dry in a steam or electrically heated oven. While partial drying is essential in the case of the very bulky ammonia precipitate, the author does not favour drying in most cases. When a dry filter paper is folded preparatory to being placed in the crucible, there is a decided risk that some of the dry precipitate will be shot away as fine dust. Indeed, with a dried silica precipitate it is difficult to avoid doing this. The author is therefore of opinion that, in addition to being a waste of time, complete drying may also result in slight losses which will not occur if the precipitate is ignited while still moist. In the majority of cases there is no necessity for drying a precipitate, provided the operation of ignition is commenced correctly.

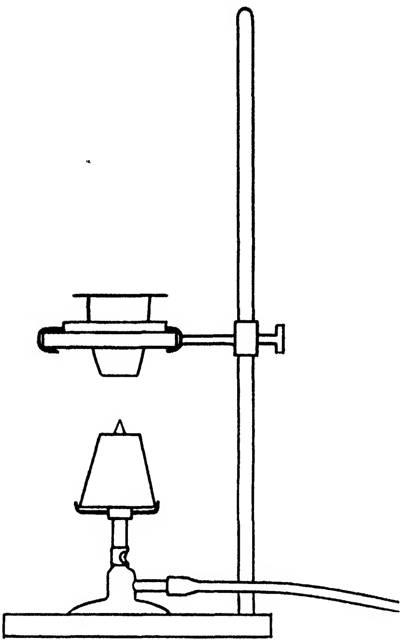


FIG. 6.—IGNITION OF PRECIPITATES: CARBONIZATION OF FILTER PAPER.

The filter and precipitate having been placed in the crucible,* the lid is put in position, the crucible supported in a silica triangle, and a luminous flame about ½ inch high is set 2 inches below the bottom of the crucible. Steam will escape gently from the crucible but there should be no spattering or boiling going on inside. In the course of ten minutes, if the precipitate is a small one, the issue of steam will stop. The flame may then be raised so that it is about 1 inch in height when, after a few minutes, smoke

* If there is a line on the funnel at the top edge of the filter due to the precipitate creeping up (calcium oxalate is particularly prone to do this), it may be rubbed off with a scrap of filter paper on the end of a spatula and added to the crucible for ignition.

will gently escape from the crucible. This smoke must not be allowed to catch fire. At the end of five to ten minutes the evolution of smoke will reach its zenith and thereafter rapidly dwindle away. At this point the lid is carefully removed and the crucible tilted at about 45° Provided the carbonization has not been carried out too rapidly, the blackened and completely carbonized paper will then commence to glow as the carbon slowly burns. All draughts must be carefully avoided at this stage. The size of the flame is gradually increased and more air admitted to it as the carbon is removed. *The luminous flame must not be allowed to touch the crucible nor should the crucible be enveloped in the bunsen flame at this stage.* In other words, the carbon is incinerated with the crucible gradually becoming red-hot on its underside. Paradoxically, as it may appear to the beginner, the slow carbonization and gentle heating result in the quickest incineration of the carbon. If carbonization is carried out very rapidly at high temperature, complete removal of the carbon may prove very difficult and tedious.

The carbon having been completely incinerated, the flame is removed for a moment and used to burn the carbon off the underside of the lid, which is held with the blackened side away from the flame. This operation takes only thirty seconds or so, after which the crucible is set vertically and the lid replaced, *but not entirely covering the crucible.* The crucible is then ignited at a bright red-heat, the flame being arranged so that the inner blue cone does not touch the platinum and the crucible is not wholly enveloped by the flame. For stronger ignition a change-over is made later to a Teclu burner and, for still higher temperatures, the blast Méker is employed. In blasting it is particularly important that the flame should not wholly envelop the crucible. If it does, and the lid is quite closed, a reducing atmosphere will result inside the crucible with possibly some reduction of the contents. At the end of an ignition the lid should be removed for a moment so that any gases present, such as steam, carbon dioxide, etc., escape and are not left to be absorbed by the residue as it cools in the desiccator. Until experience has been acquired as to the

length of time required for ignitions, the crucible and residue should be re-ignited for a further ten minutes after weighing, and then re-weighed to insure that the ignition is complete. If the weight is not constant, further ignition is necessary.

After ignition a platinum crucible should be left in a desiccator in the balance room for twenty minutes before weighing. A porcelain or silica crucible will require thirty minutes before weighing. Sintered-glass crucibles which have been heated to 110° C. or 130° C. will require twenty minutes in the desiccator. With good quality filter paper the weight of the ash may be neglected.

Use and Care of Platinum Apparatus.—Platinum must not be heated in contact with other metals. For this reason the usual gun-metal tongs must have platinum tips fitted to them. Platinum must not be handled by any tongs not so equipped or a stain will result.

Crucibles must not be in contact with the inner reducing cone of the bunsen flame, neither should luminous or sooty flames play on them, nor filters be allowed to burst into flame during incineration. Such maltreatment gives rise to a carbide of platinum which renders the crucible brittle and liable to crack.

Compounds of readily reducible metals, phosphides, arsenides, and sulphides are to be avoided. Small quantities of sulphides are sometimes met in rock analysis, and these are dealt with in Chapter VIII. (*e*). The oxides of sodium, potassium, lithium, and barium, as well as their hydroxides, nitrates, nitrites, and cyanides, attack platinum strongly. Care must be taken never to add nitric acid or a nitrate when hydrochloric acid or chlorides are present, otherwise chlorine liberated will attack the platinum vessel.

Platinum is also very slightly soluble in a number of the operations of silicate analysis. It is more marked in the sodium or potassium pyrosulphate fusion where several mg. of platinum are usually dissolved, according to the temperature used and the length of duration.

Platinum vessels should be kept clean by periodical burnishing, carried out by means of sand rubbed over while damp with the fingers or a cloth. This sand *must have rounded grains*, as in a well-worn, wind-blown sand, and should be

quite fine, say 75-100 mesh. The majority of stains on platinum can be removed by prolonged heating on a water-bath with concentrated hydrochloric acid. If a crucible becomes so badly stained that acid fails, a small fusion with sodium pyrosulphate for about five minutes will clean it. The bulk of the salt is poured out on to a stone slab while molten, and the remainder is soon dissolved in hot water containing a little sulphuric acid.

CHAPTER VI

NORMAL METHODS FOR SILICATE ROCKS

(1) Main Portion

Introduction

In the main portion, silica, the ammonia precipitate, lime, and magnesia are determined. The ammonia precipitate, which, after ignition, consists of the mixed oxides, may be utilized further, by means of a pyrosulphate fusion and subsequent solution, for the determination of total iron and titania. If preferred, the total iron and titania may be determined on a separate portion, when the residue of mixed oxides is rejected.

In briefest outline, the methods employed are, viz., décomposition of the silicates by fusion with sodium carbonate and subsequent solution in acid, the separation of silica by dehydration, the precipitation by ammonia of iron and alumina together with a number of minor constituents, the precipitation of lime as oxalate, and ending with precipitation of magnesia, usually as the double salt magnesium ammonium phosphate. At more than one stage alternative methods present themselves. Thus by the use of bromine water, manganese in the great majority of rocks may be brought down almost entirely with the ammonia precipitate. This simplifies matters, as otherwise those portions of the manganese carried down with the lime and magnesia will each have to be determined. The possibility of using the mixed oxides for total iron and titania, or alternatively their determination in a separate portion, has already been mentioned. Lastly, when magnesia is present in only small amount, it will sometimes be an advantage to use the hydroxyquinoline method. The relative advantages

and disadvantages of these methods vary with the conditions of work, and further guidance will be given in the sections concerned.

Diagrammatically, the outline scheme for the main portion is as follows :

Silicate Rock or Mineral
|
Fusion with Na_2CO_3
|
Evaporation with HCl
|
SiO_2 (dehydrated). — NH_4OH
|
R_2O_3 (ammonia ppte.) — $(NH_4)_2C_2O_4$
|
CaO (CaC_2O_4) — $(NH_4)_2HPO_4$
|
MgO ($MgNH_4PO_4$) — Discard.

Further treatment of ignited ammonia precipitate :

R_2O_3 ppte.
|
Pyrosulphate fusion
|
Aqueous soln.
|
Reduction with H_2S
|
Titration of iron with $KMnO_4$
|
Addition of H_2O_2 and colorimetric comparison for TiO_2

Weighing out Main Portion. — 1-1½ g. are used, but much time is saved on the calculations, and results can be read off directly in percentages, if exactly 1·0000 g. is weighed out. This takes only two to three minutes longer, and the advantage of ready comparison of results when a series of analyses is being run is considerable. A clean 35 g. crucible is ignited to a red heat and cooled in a desiccator. It is then placed on the balance pan by means of nickel-plated steel tweezers kept in the balance case for this purpose. The

lid is best placed under the crucible during this weighing. The 1 g. sample is then weighed directly into the crucible.

Mixing with Flux.—The flux used (anhydrous A.R. sodium carbonate) is added about 1 g. at a time and carefully mixed with the rock powder in the crucible by means of a small stirring rod. With rocks high in silica, such as granites and rhyolites, 5-6 g. of sodium carbonate will suffice, but with more basic rocks this amount must be increased and 10 g. may be regarded as the limit for ultrabasic rocks and ferromagnesian silicate minerals. If in doubt as to the basicity of the material for analysis, use 8-9 g. of sodium carbonate. The size of the crucible should be such that it is not more than half filled with the powder.

Fusion.—The crucible is closed and placed in a silica triangle fitted with nickel wire. After comparatively gentle heating for two to three minutes to drive off any moisture, the full heat of the Teclu burner is applied. At the end of a few minutes the flux commences to fuse and considerable effervescence takes place. There is no point in removing the lid at this stage to see how things are going on, for a slight loss by spattering may result. It is better to leave the crucible well alone for the first fifteen minutes, after which the lid may be opened a little to admit air, and the heating is continued until the melt is quite calm. This stage will be reached in about twenty to thirty minutes from the commencement, the actual time depending on the efficiency of the burner and of the mixing.

When the melt has been calm for several minutes, the crucible is transferred to the blast Méker burner run at full power. Further effervescence will then take place in the melt, but only for a few minutes. If, however, the crucible is transferred to the blast burner too soon, the melt will boil over, ruining both the analysis and the silica triangle. As soon as the melt has become calm, the lid is removed with care so as not to lose the drop of melt usually adhering to its under surface, and the crucible is given a gyratory motion so that the melt swirls up around the sides incorporating any incompletely attacked material there. Care is required in this operation, but the necessary skill is soon acquired.

The lid is removed, and the melt adhering to it is dissolved

by a jet of hot water caught in a 6-inch platinum dish.* A few drops of dilute hydrochloric acid are used to make sure that the last traces of adhering melt are removed from the lid.

During this minute or two the crucible has remained without its lid over the blast. This does no harm and tends to insure complete oxidation. The crucible is removed from the blast, without delaying to turn out the flame, and is carried with due care to the sink where the melt is made to swirl around so that as it solidifies it forms a thin even layer covering most of the inside of the crucible. As soon as the melt has completely solidified, the crucible is held in an inclined position and cooled on its outside by water from the tap, care being exercised to see that none goes into the crucible. This sudden cooling tends to crack the melt away from the platinum and assists in the general disintegration of the mass.

The crucible is then stood in the platinum dish, a few drops of alcohol added, followed by careful addition of 1 : 1 hydrochloric acid, and the whole covered with a large clock glass. As the reaction becomes less vigorous, the contents of the crucible are stirred and a little more acid added. After one or two additions of acid the crucible will be full, when it is emptied into the dish, rinsed out once with hot water, a few drops of alcohol added, and the process repeated. This is by far the most rapid way of removing the melt from the crucible, but the addition of alcohol is essential, as otherwise the acidification of manganates present will free chlorine, which in turn will attack the platinum.

When the last traces of the melt have been dissolved, the crucible is raised on the glass rod and held between two fingers of the left hand, while it is washed inside and out by a jet of hot water from a wash-bottle held in the other hand. Finally, the crucible is rubbed over inside and outside with a feather to remove traces of gelatinous silica which may still be adhering, and again washed with hot

* If a large platinum dish is not available, a 9-inch porcelain dish with a black glaze on its inner surface may be substituted, but at the loss of considerable time in the evaporations and with increased difficulty in removing the silica. It is difficult to see adhering silica on a white glazed dish.

water. The dish is then placed on a water-bath with porcelain rings and the contents evaporated to dryness.

Silica

General Considerations.—Silica is acidic in its reactions, so that if a silicate is fused with an alkali such as caustic potash, caustic soda, or the carbonates of these metals, a double reaction takes place with formation of the alkali silicate and either the hydroxides or carbonates of the other metals, according to the flux used. The alkali hydroxides when fused attack platinum, so that they can be used only with a nickel or iron crucible — or better still, one made of silver — in special cases where the incorporation of material from the crucible is of no consequence. For the main portion, either sodium or potassium carbonate, or fusion mixture (an equimolecular mixture of the two) may be used. Potassium carbonate is too deliquescent, is liable to absorb sulphur dioxide and hydrochloric acid fumes from the laboratory atmosphere, and requires dehydration immediately before use. Fusion mixture suffers rather less from these defects and is more readily fused than sodium carbonate. Anhydrous normal sodium carbonate, however, is most suitable for the main fusion, for it is obtained pure more easily, is cheaper, and does not absorb moisture and fumes so readily as the potassium salt or mixtures containing it. Further, it has a great advantage in that its comparatively high melting point of about 800° C. tends to insure the use of a sufficiently high temperature for the complete decomposition of silicates.

Carbon dioxide is evolved during the main fusion and this causes effervescence. Although the melt may have become calm, when it is blasted, some further release of carbon dioxide invariably occurs. This is probably due not only to completion of the reaction of the sodium carbonate on the silicates but also to breakdown of the akaline-earth carbonates with the formation of more complex silicates and perhaps aluminates. It is incorrect to assume that the alkaline-earth metals, magnesium, iron, etc., are all present

as carbonates after fusion at high temperature, but the fact remains that the melt is then completely decomposed by dilute acid with release of gelatinous silica.

The gelatinous silica referred to above is in fact a hydrogel of silicic acid which is quite appreciably soluble. The silica is rendered insoluble only by thorough dehydration. This, however, is not achieved so easily as may at first be imagined, for, if after evaporation on the water-bath the apparently dry residue is ignited or baked, the silica tends to re-combine with the other constituents, particularly the magnesia. This would result in a considerable amount of silica passing through the filter as a soluble silicate with consequent complications. It has been shown that 130° C. is the highest temperature allowable for drying the silica. In practice, therefore, the acid solution and silica are evaporated to dryness over steam, drenched with concentrated hydrochloric acid, re-dissolved in water, and the insoluble silica filtered off. One such evaporation is insufficient for work with any claim to accuracy, as in the most favourable circumstances several milligrams of silica pass through in solution, and usually more than this. A second evaporation is thus essential, and for work of the highest accuracy a third evaporation may sometimes be necessary.

The need for the most thorough drying of the residue on the water-bath is paramount, otherwise the silica determination will be decidedly low. Any silica which passes through will be precipitated with the other constituents, particularly the ammonia precipitate, so that they will be correspondingly high. The silica is determined by difference in weight after expulsion as silicon tetrafluoride (SiF_4).

Drying and Separation of the Silica.—As in the course of evaporation the solution reaches a small bulk, a crust develops over it. This should be broken up from time to time, together with the solid salts on the sides of the dish, to assist the process of drying. The salts are frequently turned over with a stout glass rod, the end of which has been rounded off in a flame. By the time the last of the liquid has gone, the residue will be a deep golden-brown or yellow according to the amount of iron present, but, as the drying continues, the colour pales, and when the smell of hydro-

chloric acid can no longer be perceived, it will be nearly white. The residue should be left to dry for a further hour after this stage, and the whole process will have occupied all the working hours of one day.

The dish is removed from the water-bath and the contents drenched with concentrated hydrochloric acid, 10-15 c.c. being used. With rocks or minerals high in titania, even more acid may be used with advantage. After being allowed to stand for five minutes, a jet of cold water is used to wash the material away from the sides of the dish, and more is added until most of the salts go into solution on stirring. Most of the liquid is filtered through a No. 41 11 cm. paper, and more water is added to complete the solution of the salts. The silica is carefully transferred, still with cold water, to the filter, but no attempt is made to remove the last traces adhering to the dish. The silica is then washed with nearly boiling water until free from chloride, as shown by testing the washings with dilute silver nitrate containing a little nitric acid. About eight to ten washings are usually required, and the filtrate should not be tested before the seventh or eighth. On what is expected to be the last washing, 5 c.c. or so of filtrate should be tested, and, if there is the slightest turbidity, further washings are called for.

The filtrate is then returned to the platinum dish, and the whole process of evaporation and filtration repeated, using a 9 or 11 cm. paper. If the first silica precipitate is filtered off at the end of the working day, the second evaporation can look after itself overnight. The silica of the second or third evaporation is always less pure than the first, and, with rocks high in iron, a little platinum may be taken up from the dish. The effect of this is usually insignificant, and in any case it will not affect the silica but be precipitated mainly with the lime. The washing of the second silica precipitate must be as thorough as the first, but usually occupies much less time on account of the smaller bulk.

The 35 g. crucible used for the main fusion, after being ignited and weighed, is used for the ignition of the silica, the precipitates being ignited together while still moist. This ignition must be carried out without undue haste or the silica will not be obtained snow-white, as should be the

case.* Once the silica is white, it is heated over a Teclu burner for twenty minutes and finally over the full blast for ten minutes. The ignited silica is somewhat hygroscopic, so that the weighing should not be unduly prolonged.

The silica is carefully moistened with a drop or two of cold water (directed on the side of the crucible to prevent "dusting"), several drops of 50 per cent. sulphuric acid are added, and the crucible is two-thirds filled with A.R. hydrofluoric acid. The uncovered crucible is then left over a small flame so that it evaporates steadily but without boiling over or spurting. At the final stage, as shown by cessation of frothing, the flame is increased somewhat to drive off the sulphuric acid, the crucible is half covered with its lid, and blasted for ten minutes to remove the last traces of sulphuric acid and silicon tetrafluoride and to oxidize the residue fully.

The loss in weight after this operation represents the amount of silica removed, though a small correction is required for the insoluble residue left by the hydrofluoric acid. Neglect of this correction will mean that the figure for silica will be slightly low and the alumina correspondingly high. The correction is therefore added to the silica and subtracted from the R_2O_3. A common figure for A.R. hydrofluoric acid is 0·0025 per cent. of insoluble residue. If, then, 20 c.c. are used for the evaporation and 1 g. of rock was taken for the main portion, the correction amounts to about 0·0005 g. or 0·05 per cent. in terms of the final result. This is well within the limits of experimental error but, for work of the highest standard, the correction should be made. With ordinary "re-distilled" grade of hydrofluoric acid the correction will be more important.

After weighing, the crucible with its small amount of residue is carefully preserved in this condition and is used for ignition of the ammonia precipitate obtained by either of the methods described in the next section, "R_2O_3."

* If the silica is ignited too rapidly in the early stages, a black colour is imparted which is extremely difficult to remove. K. A. Krieger and H. S. Lukens have shown that this effect is due to the formation of silicon carbide rather than to a mechanical darkening by carbon (*Ind. Eng. Chem.* 1936, 8, 118).

"R_2O_3"

General Considerations.—The principal constituents of the ammonia precipitate are the hydroxides of iron and aluminium, but titanium, phosphorus, vanadium, zirconium, and rare-earths are also precipitated here. The precipitation of manganese, nickel, cobalt, copper, etc., is only partial. Phosphorus is precipitated as the phosphates of the other metals. If, therefore, phosphorus is in excess of the total iron, alumina, etc., it will also bring down the requisite amount of calcium as phosphate. This may be prevented by the addition of a known amount of iron but, except in phosphatic rocks, this set of circumstances will rarely be encountered.

The addition of too much ammonia leads to re-solution of some of the alumina, but the best conditions for precipitation have been established and are those given in the instructions which follow. The requisite value of pH corresponds to the colour change of methyl red from red to yellow. Owing to the low solubility of magnesium hydroxide, a certain concentration of ammonium chloride is required to prevent its co-precipitation. Nevertheless, the first precipitation of ammonia inevitably carries down with it some lime and magnesia so that re-precipitation is always necessary. The separation is then very efficient and tests on rocks with very high lime or magnesia show that a third precipitation is scarcely necessary.

The precipitation of titania and phosphorus is complete, but not that of manganese. A little of the manganese which passes on comes down with the lime, but most of it is precipitated with the magnesia as phosphate, and is ignited subsequently to the pyrophosphate $Mn_2P_2O_7$.

The use of bromine as described by Holt and Harwood* insures precipitation of the bulk of the manganese by ammonia, provided the manganese content is not too high. Two courses, therefore, present themselves to the analyst : either he allows the manganese to take its own course and come down in the three stages just indicated or, by the use of bromine, he insures that it is precipitated with the ammonia precipitate. If he adopts the first course, it will be

* *Mineralog. Mag.*, 1928, **21**, 318.

necessary to re-dissolve the lime and magnesia precipitates and determine their manganese contents colorimetrically whence, by subtraction of the sum of these from the total manganese present, that precipitated by ammonia is obtained and the alumina can be suitably corrected. The two additional manganese determinations take an appreciable time and the use of the lime precipitate for subsequent determination of strontia is rendered awkward. On the other hand, the use of bromine adds only two or three minutes to the whole operation and, if conducted with care, is reasonably accurate. The bromine method has a slight drawback in that the use of a platinum dish for the subsequent evaporation of the acidified filtrate is inadmissible, owing to the presence of free bromine, and a porcelain dish has to be used. On the whole, however, the bromine method, on account of its speed and simplicity, is best adapted for beginners and is suitable for the great majority of silicate rocks. For work of the highest accuracy it is perhaps better to determine the manganese in the lime and magnesia. In correcting the alumina for the small amounts of manganese usually present in rocks, it is probably sufficiently correct to assume that, after ignition, whether or not bromine has been used in the ammonia precipitation, the manganese has been weighed as Mn_3O_4. Care has to be taken to keep the liquid well stirred during precipitation in order to avoid local excess of ammonium hydroxide with possible re-solution of alumina.

Practical Hints.—The gelatinous ammonia precipitate is generally more or less bulky so that its filtration and washing is often inclined to be tedious. Filtration usually proceeds best when the ratio of iron to alumina is high, conditions which unfortunately occur only infrequently. A filter paper of ample dimensions (12·5 or 15 cm.) is used and the liquid to be filtered is kept just boiling. Between each addition of liquid to the filter, the funnel is kept covered with a watch-glass with its convex side downwards. This not only keeps out the dust during a long filtration but, in cold weather especially, prevents the speed of filtration being reduced by rapid loss of heat. Further time may be saved by use of the special Jena funnel (see p. 41).

At the end of the first filtration and after removal of the

precipitate by a jet from the wash-bottle, the contaminated half of the paper is torn off and added to the acid solution of the first precipitate. It is well stirred as the liquid is heated and soon forms a good pulp. The liquid is more liable to bump when pulp is present and should therefore be stirred the whole time, but the speedier filtration and washing resulting after the second precipitation may often save half an hour. Stirring to prevent local excess of ammonia during precipitation is still more important when pulp is used. The precipitate requires to be well drained and partially dried before ignition, otherwise the liquid contents of the precipitate will boil over or spurt at the commencement of the ignition, with the introduction of serious error.

PROCEDURE.—(*a*) WITHOUT THE USE OF BROMINE.—**To the combined filtrates from the silica, 5 c.c. of concentrated hydrochloric acid and one 7 cm. 41 Whatman filter paper are added. The liquid is brought to the boil with continual stirring so that the paper may form a good pulp by the time boiling point is reached. Ammonia (0·880 sp. gr. diluted in the proportion 1 : 1) is then added gradually from a tap funnel, with constant stirring, until the liquid assumes a brown colour and precipitation is on the point of commencement. The flow of ammonia is then reduced to about one drop every two or three seconds. When precipitation is nearly complete, a drop of the liquid is tested on a strip of methyl red paper. While the test is being applied, the addition of ammonia should be stopped, unless it is being made at a very slow pace. The moment a drop turns the methyl red paper yellow, precipitation may be considered complete. The sides of the beaker are swilled down, and another drop of ammonia may then be required. Three more drops of ammonia are then added, the liquid boiled for one minute, and filtered through a 12·5 or 15 cm. No. 41 Whatman paper. With experience, the completion of the precipitation can be gauged by the appearance of flocculation, but the drop test should never be omitted. The tests should be made with a thin rod, using only small drops. One drop is used for each test, and after practice not more than three such tests will be required.**

The beaker is swilled out once more with the hot 2½ per cent. ammonium chloride wash liquid but no attempt is made to remove the last traces of precipitate adhering to the sides. The precipitate is allowed to drain, and then washed three times with boiling ammonium chloride wash liquid, the filter being well drained between each washing. The filtrate is transferred and rinsed into a large platinum dish or a 9-inch porcelain dish, a few drops of methyl orange added, the liquid acidified with strong hydrochloric acid and a few c.c. in excess added. The dish is then put to evaporate on the water-bath.

The precipitate is transferred by means of a jet of hot water to the soiled beaker in which the original precipitation was made. 5-10 c.c. of concentrated hydrochloric acid are introduced, according to the amount of magnesia expected, and the soiled half of the filter paper is also added. The volume is made up to 250 c.c., the hydroxides re-precipitated, filtered, and washed with hot ammonium chloride as before. At the end of the third washing, the filtrate is added to the first one, which by this time will have evaporated somewhat. The combined filtrates are evaporated to about 200-300 c.c., according to the amount of lime and magnesia expected. The transference of the precipitate from the beaker will have been more complete the second time owing to the greater bulk of pulp. The last traces of precipitate are easily removed by means of a tiny wad of filter paper on the end of a rod.

Meanwhile a wash-bottle containing ammonium nitrate is brought to the boil and kept in readiness. The precipitate is washed with this boiling solution until the filtrate is free from chloride. With acid rocks giving a small precipitate, seven to eight washings are usually sufficient, but, with intermediate and basic rocks, eight to ten, and sometimes twelve, washings will be needed, involving the use of 500 c.c. of the second wash liquid. When fifty drops of filtrate fail to produce any visible turbidity with silver nitrate solution containing some free nitric acid, the washing may be regarded as complete, and the precipitate free from sodium.

(*b*) USING BROMINE.*—The procedure under (*a*) is followed with the following modifications. Saturated bromine water

* E. V. Holt and H. F. Harwood, *Mineralog. Mag.*, 1928, 21, 318.

is added in addition to ammonia. Tap funnels containing the two reagents are fitted side by side over the beaker and, as soon as the solution boils, ammonia is added until the liquid turns a reddish-brown colour. At this point the addition of bromine is commenced, the two solutions being run at relative speeds which will keep the solution just alkaline while well stirred. As soon as the whole of the bromine water has run in, the rate of addition of ammonia is reduced and the precipitation of the hydroxides is made in the usual way. When, after filtration and washing, the precipitate is re-dissolved in acid, it is advisable to add 2 c.c. of hydrogen peroxide to insure complete solution of the manganese.

The same procedure is followed on re-precipitation. *The acidified filtrate, however, must not be evaporated in a platinum dish or the bromine set free will result in a serious attack on the metal.* A 9-inch porcelain dish is quite satisfactory.

GENERAL.—The bromine water and ammonia react to form ammonium hypobromite, a powerful oxidizing agent which precipitates the manganese as oxide (Mn_3O_4).

IGNITION OF THE PRECIPITATE.—The precipitate is carefully drained, but even so it will generally hold too much liquid to allow of immediate ignition and should be partially dried in a steam oven. When still slightly moist, it is transferred to the 35 g. platinum crucible that has been retained, complete with small residue, from the volatilization of silica (p. 55) and is ignited, first on a bunsen, then over a Teclu burner, and finally for twenty minutes over the full power of the blast. The lid of the crucible should not be altogether closed during the blasting. It is important, too, that the crucible be allowed to lose its red heat before the desiccator lid is closed, otherwise, when opened for weighing, the inrush of air is liable to blow some of the light precipitate right out of the crucible. This may happen, of course, with any residue but it is particularly prone to occur with the ignited R_2O_3 precipitate.

Keep the residue in the crucible until it has been decided which method will be adopted for the determination of total iron and titania.

Lime and Strontia—Lime is always precipitated from ammoniacal solution as the oxalate. Most of the strontia

is precipitated at the same time and, unless it is separately determined, the figure for CaO will include most of the SrO. In the great majority of cases, the error due to non-determination of strontia is a few hundredths of one per cent., though occasionally it may reach 0·20 per cent. or more. The method used for the separation of strontia depends on the insolubility of dry strontium nitrate in strong nitric acid.

Ammonium oxalate is the salt generally used for the lime precipitation, a sufficient amount of ammonium chloride being present to prevent co-precipitation of magnesia. In practice, some magnesia is always precipitated with the lime. It follows that a re-precipitation is always desirable and, indeed, essential when much magnesia is present. On account of this marked tendency for magnesia to be precipitated with the lime it is probably preferable, in all cases, to use oxalic acid and carefully neutralize it *in situ*. Methyl orange is the most suitable indicator but, after standing a little while, the pink colour begins to return, when a few drops of ammonia must be added. The aim should be to have several drops of dilute ammonia in excess to keep the indicator just yellow. Several further additions of ammonia may be required during the first hour or so after the precipitation.

In the author's experience, it is quite noticeable when very small amounts of lime are to be precipitated — as in micas — that precipitation is accelerated by keeping the liquid gently boiling for half an hour before putting aside to cool. With only a few tenths of one per cent. of lime, the precipitate may not appear for the first five or ten minutes. It should never be concluded that lime is absent unless no precipitate has appeared after standing at least four hours.

The general practice is to ignite the oxalate precipitate to the oxide. An intermediate stage in this ignition is the formation of carbonate and suggestions have been made that ignition to the carbonate is to be preferred on the grounds that it is much less hygroscopic than quicklime. Unless the temperature is accurately controlled by the use of a pyrometer, the resulting residue will inevitably be of uncertain composition. Moreover, it can readily be shown,

as has been pointed out by Hillebrand-Lundell (p. 499), that there is no appreciable error in the weighing of a well-blasted lime residue provided that the weighing is expeditiously carried out immediately after removal of the crucible from the desiccator.

Directions.—**The acid solution, which should have a volume of 150-300 c.c., according to the amount of lime present, has added to it 2 g. of A.R. ammonium oxalate, or the equivalent of oxalic acid, and several drops of methyl orange. The solution is brought to boiling point and ammonia (1 : 1) added from a tap funnel, with stirring, until the pink of methyl orange is just discharged. The liquid will now be turbid with white precipitate if much lime is present. Just sufficient ammonia is added to bring a yellow tint to the methyl orange. The burner is then turned down until the heat is just enough to keep the liquid boiling, and a rod is used to prevent bumping. The liquid is kept gently boiling for half an hour, several more drops of ammonia being added from time to time whenever the indicator shows it to be necessary. The beaker is then put aside to cool and allowed to stand for at least four hours, preferably overnight.**

The liquid is filtered through a 11 cm. No. 40 paper and washed with a 0·1 per cent. solution of ammonium oxalate. Sometimes colourless crystals will be observed together with the calcium oxalate due to excessive addition of ammonium oxalate or oxalic acid, or to the precipitation of magnesium oxalate which is only sparingly soluble. They are of no consequence as they re-dissolve fairly readily in the wash liquid.

Precautions against Incorporation of Platinum in the Analysis.—If for any reason platinum has got into the analysis — and it often does in the case of the more basic rocks — its presence will have been indicated by a slight greenish-grey sludge or deposit forming at the bottom of the dish towards the close of the evaporation of the filtrate and washings from the R_2O_3 precipitate. If present in appreciable amount, this material, which is probably a platinum ammine, will colour the lime precipitate so that after filtration it appears as a dirty white. If such a precipitate of calcium oxalate is ignited to the oxide, the residue will be light or dark grey on account of the platinum being reduced to the

metal; after such treatment platinum is insoluble in acid. Ignition, re-solution in acid, and re-precipitation, therefore, form a very rapid and effective way of removing any platinum present. It should be observed that mere re-precipitation of the calcium oxalate is ineffective.

RE-PRECIPITATION AND IGNITION TO OXIDE.—**On re-precipitation of the calcium oxalate only 0·5 g. of oxalic acid or ammonium oxalate is required.**

The ignition is carried out in the usual manner and completed with five minutes of blasting. Prolonged blasting of lime in platinum leads to an attack on the crucible which can be shown afterwards to have absorbed some calcium. The crucible is placed in a desiccator for twenty minutes to cool and afterwards weighed as expeditiously as possible. If strontia is to be determined, the residue is kept for this purpose.

SEPARATION OF STRONTIA: GENERAL.—The separation of strontia from lime is based on the fact that dried calcium nitrate is soluble in concentrated nitric acid whereas dried strontium nitrate is insoluble. W. Noll* has shown that the method of separation of strontium from calcium by extraction of the nitrate with an ether-alcohol mixture — a method much used in the past — should be replaced by that of S. G. Rawson (1897), using nitric acid of specific gravity 1·445.† An even stronger acid of sp. gr. 1·46‡ was recommended by Rawson but, as the density of the acid is increased, the solubility of calcium nitrate is greatly diminished so that, if much lime is present, a very considerable volume of the acid will be required.

Inaccuracy in the determination of strontia is due not so much to error in the separation from lime (which tends to give high results) as to the incomplete precipitation of strontium as oxalate. W. Noll (*op. cit.*) states that the loss of strontium in the oxalate precipitate is less serious (about 3 per cent. of the Sr for an Sr : Ca ratio of 1 : 100), but increases with the Sr : Ca ratio and may reach 18 per cent. of the strontium. By adding about 0·5 to 0·1 g. of a

* W. Noll, *Zeits. Anorg. Chem.*, 1931, **199**, 193-208.
† This is the specific gravity recommended by Prof. H. F. Harwood.
‡ *J. Soc. Chem. Ind.*, 1897, **16**, 113.

pure calcium salt to the combined filtrates from the usual oxalate precipitation and re-precipitation, then precipitating this additional calcium in the usual way, the loss of strontium can be reduced to neglible proportions. The additional precipitate of calcium and strontium oxalates is united with the main one after weighing. Rawson's method also serves to free a calcium salt from small amounts of strontium.

Another method for strontia is given on p. 165. In that method, which is the most accurate available, barium and strontium are determined together on a separate sample. It takes considerably more time to carry out, however, than the method described below.

PROCEDURE.—**Carefully slake the quicklime by means of a few drops of water from the wash-bottle directed on the side of the crucible. Add sufficient dilute nitric acid to dissolve the lime, and transfer the solution without loss to a 200 c.c. Pyrex beaker, carefully rinsing out the crucible with water from the wash-bottle. Place the beaker on the outer part of a large sand-bath, or on a smaller sand-bath over a low flame, so that the solution is evaporated to dryness without boiling or spurting. When the contents of the beaker are thoroughly dry, they are carefully broken up with a glass rod while the beaker is allowed to cool. When cool, 100 c.c. of the special nitric acid of sp. gr. 1·445 are added, and all lumps are broken with meticulous care. If any compacted lumps are allowed to remain, considerable difficulty may be experienced in getting them into solution. The liquid is then alternately stirred, set aside for a time, and stirred again until all the solid has dissolved. This is best done by means of a mechanical stirrer driven by a small electric motor or hot air engine. The length of time and amount of acid required depend on circumstances, and can be gauged to the best advantage only after some experience with the method. The aim should be to use as little acid as possible, for although much acid will dissolve the calcium nitrate rapidly, it will tend also to dissolve some of the strontium nitrate. When all the solid has gone into solution, the presence of a slight opalescence will indicate strontium nitrate in suspension. It is difficult to see the strontium salt at this stage if less than 0·02 per cent. SrO is present. More than 0·10 per cent. SrO**

will cause a slight turbidity (a 1 g. sample being used in each case).

When all the calcium nitrate has dissolved, usually after some hours, and followed perhaps by standing overnight, the liquid is filtered through the special apparatus shown in Fig. 5b. This consists of a specially shaped fritted glass filter, held by a waxed cork in an ordinary filter flask. This arrangement obviates the difficulty of the nitric acid fumes attacking a rubber stopper. Even so, it is as well to have some water in the filter flask to prevent the fumes attacking the rubber exhaust tube leading to the filter pump. The liquid is filtered in this way, the residue transferred to the filter, and then washed ten times with the special acid. This washing must be done most thoroughly or the final product will almost certainly be contaminated with lime.

The washing completed, the suction is stopped, the filter removed, and the contents of the filter flask well swilled out. In case of an accident during the next step, it is as well to have all the traces of calcium nitrate swilled out. A test-tube with a piece of string tied to the end is then placed as a receiver in the filter flask, the end of the string being allowed to project outside from under the cork. The fact that the string will probably lead to slight leakage of air is an advantage rather than disadvantage in this case. Half a test-tube of hot water is then drawn through the filter in several small portions. At this stage the test-tube in the desiccator is half full, and the stem of the filter is nearly under the liquid. If the suction is suddenly stopped, some of the tap-water rushing into the filter flask will almost certainly get into the test-tube and so introduce lime. It is better to reduce the suction very slowly, watching the water-level in the filter pump. The leakage at the string and through the dry filter will allow of this. In this way, although thirty to sixty seconds may be taken in turning off the suction, there will be no rush back of tap-water.

The filter is removed, the test-tube being held up and extracted by means of the piece of string, and the contents rinsed into a 100 c.c. beaker. Two or three drops of 50 per cent. sulphuric acid are added, and the contents evaporated as far as they will go on the water-bath. An equal bulk of

absolute alcohol is added. If strontium is present in appreciable amount, it will be seen as a heavy white crystalline precipitate which hangs back at the edge of the liquid. If a light, almost flocculent precipitate is produced, it will be calcium sulphate, indicating a bad separation. It is only fair to say that beginners do not usually achieve a good separation until they have had some experience of the method.

The beaker is allowed to stand overnight, and next morning the strontium sulphate is filtered off on a 7 cm. 40 paper, washed with 50 per cent. alcohol, ignited at a low red heat, and weighed as $SrSO_4$. The purity of the product is tested with a pocket spectroscope; there should not be more than a trace of lime. If appreciable lime is present, the situation can be saved by the following procedure: Fuse the strontium sulphate with a little sodium carbonate for ten minutes, leach, filter, and wash, dissolve the residue in nitric acid, evaporate to dryness, and then treat the dried nitrates in the same way as above, though a smaller quantity of the special nitric acid will be required.

Magnesia

General.—Magnesia is usually precipitated as magnesium ammonium phosphate in the filtrate and washings from the calcium oxalate by the addition of a soluble phosphate in the presence of an excess of ammonia. The precipitate is ignited and weighed as magnesium pyrophosphate. If the amount of magnesia is known to be small, then it may be precipitated and determined more rapidly by means of the reagent 8-hydroxyquinoline; the resulting precipitate is, however, very bulky, so that the method should be used only when less than 2-3 per cent. MgO is expected. Whichever method is used, the precipitation of small amounts of magnesia tends to be incomplete when considerable amounts of ammonium salts are present, which is invariably the case. The ammonium salts have, therefore, to be removed.

Removal of Ammonium Salts.—This is always carried out in a porcelain dish (9-inch). The solution is acidified and evaporated to dryness or to a small bulk. *The next operation*

has to be performed in a fume cupboard. Add to the cold dish 100 c.c. of concentrated nitric acid (or 3 g. for every gram of ammonium chloride); an excess does no harm. Replace the covered dish on a water-bath, or better over a steam jet, and warm the contents gradually. A violent reaction sets in with evolution of nitrous fumes. As it begins to subside, a little more steam is turned on until the reaction is complete, when the cover glass is rinsed into the dish, and evaporation continued to dryness again. If the 8-hydroxyquinoline method is to be used, it is particularly important to see that all nitric acid has been removed. The salts are dissolved in hot water, to which a few drops of hydrochloric acid are added, and then rendered slightly alkaline by ammonia.

DETERMINATION OF MAGNESIA AS MAGNESIUM PYROPHOSPHATE.—The volume of the solution (the filtrate and washings from the lime) should not exceed 600 c.c.; if it does, it should be acidified and evaporated to a smaller bulk. If only a small amount of magnesia is known to be present, ammonium salts should be destroyed and the solution made up to 250-300 c.c. A concentrated and slightly ammoniacal solution of diammonium phosphate (2 g. for each 100 c.c. of solution) is added, followed by strong ammonia (sp. gr. 0·880) (10 c.c. for each 100 c.c. of solution). The ammonia is added in a thin stream while the liquid is well stirred. Care should be taken to avoid touching the sides of the beaker with the rod or the precipitate will adhere very strongly to the parts which have been rubbed. With average amounts of magnesia the precipitate of magnesium ammonium phosphate can be seen forming during the next minute or two. With small amounts a slight cloudiness is all that may be seen for some time. If, however, too much ammonia is added, large quantities of other salts present are thrown down. These can, of course, be re-dissolved during filtration and washing, but this involves a great deal of extra washing. The beaker is then put aside to stand overnight. In the case of very small amounts of magnesia the liquid should stand from twenty-four to forty-eight hours.

After standing, the liquid is filtered through a 9, 11, or 12½ cm. No. 40 Whatman filter paper, according to the bulk

of liquid and precipitate, and washed with a 5 per cent. solution of ammonia until free from chloride. On account of some co-precipitation of sodium salts it is highly desirable, especially if more than say 5 per cent. of MgO is present, to re-precipitate. To this end, hot dilute hydrochloric acid (warmed in the original beaker) is poured in several lots through the filter paper and collected in a 250 c.c. beaker. The filter is then washed several times with water. Dilute to 50-100 c.c. according to the amount of magnesia present. Add 0·1-0·3 g. of diammonium phosphate, dissolved in a few c.c. of water to which a little ammonia has been added. Add ammonia drop by drop from a tap funnel with constant stirring until the liquid is alkaline and most of the magnesia is precipitated. Then add 5 c.c. of strong ammonia for each 100 c.c. of the liquid. Allow to stand overnight before filtering. Filter through a No. 40 paper and wash with cold dilute ammonia (5 : 95) until free from chloride. Particular care is required to ascertain that all the precipitate has been removed from the beaker and stirrer.

The paper and precipitate are ignited wet, but with particular care to remove as much as possible of the carbon at a temperature below faint red heat. If carbonization is carried out too rapidly, some phosphorus will be freed by reduction and ruin the crucible. On the completion of carbonization the temperature is gradually raised to the full heat of the bunsen flame. After twenty minutes the crucible is transferred to the blast Méker for ten to fifteen minutes, the air and gas supply being adjusted to give a weak blast of 1,100°-1,200° C. If this blasting is not carried out, some $Mg(PO_3)_2$ may remain in the residue as the result of a little $Mg(NH_4)_4(PO_4)_2$ being formed during precipitation of the magnesium. The precipitate cannot be blasted to constant weight for the $Mg_2P_2O_7$ slowly loses P_2O_5 on prolonged blasting. If the temperature of the blast is too high the $Mg_2P_2O_7$ may be fused but, although this will not effect the accuracy, the residue will be removed but slowly by hot acid. Sometimes the residue fuses at a lower temperature than usual, as low as 1,000° C., in which case the presence of small amounts of foreign phosphates, such as calcium phosphate, is indicated.

Treatment of the Ammonia Precipitate

General Considerations.—The ignited and weighed ammonia or "R_2O_3" precipitate, after being brought into solution by means of a pyrosulphate fusion, may be utilized for quite a number of determinations such as : residual silica (which has been weighed with the R_2O_3 and would otherwise be returned as Al_2O_3), iron, titania, phosphorus, manganese, rare-earths, etc. In practice, however, it is always better, except in the case of iron and titania and residual silica, to determine these constituents on separate portions, and it is only when there is a serious shortage of material for analysis that resort is made to such methods.

The case of iron and titania is different, there being little to choose between use of the R_2O_3 precipitate and determination on a fresh sample. In the author's experience, and observations of students' work, very inaccurate results may often result from the determination of total iron and titania on a separate portion. The attack of hydrofluoric and sulphuric acids usually leaves a small black residue of ilmenite, tourmaline, rutile, etc. (containing most of the titania present) which has to be decomposed by fusion with sodium carbonate. This decomposition is not so easy to carry out in an open crucible as may be supposed, particularly if the grinding of the rock powder has not been extremely thorough, and the result is that some iron and much titania may be missed, with a correspondingly high return for alumina. Such a combination of errors is, of course, serious in the extreme, especially in connection with geological work. But unless a careful watch is kept for any dark insoluble residue when the sodium carbonate melt is dissolved in dilute sulphuric acid (see p. 76), some error on this account is very liable to occur.

A drawback to the use of the R_2O_3 precipitate is that the pyrosulphate fusion admittedly causes some loss of platinum from the crucible in which the fusion is carried out. The platinum can be removed as sulphide, so that it causes no appreciable error in the analysis, but the loss of platinum resulting in the somewhat early need for re-blocking the crucible is a factor which may become important

in an educational institution. With experience, and care in regulating the temperature of the fusion and the amount of pyrosulphate used, the loss of platinum can usually be kept down to 2-3 mg. in most cases, only reaching 6-8 mg. in ultra-basic rocks yielding 30 per cent. or more of R_2O_3.

A strong argument in favour of the adoption of pyrosulphate fusion for total iron and titania is that it immediately reveals whether any appreciable amount of silica has passed through in solution and has been thrown down with the ammonia precipitate. Even after two thorough separations for silica, a few flecks of this substance may sometimes be seen after solution of the melt from the pyrosulphate fusion. If the silica is appreciable in amount, it can be separated and the necessary correction made. Hence, using this method, one separation for silica will sometimes be legitimate for rapid work.

During fusion, the pyrosulphate gradually loses sulphur trioxide, which attacks the R_2O_3 oxides, converting them to the corresponding sulphates which are soluble.

PYROSULPHATE FUSION: PROCEDURE.—**Lumps of fused sodium pyrosulphate are used in preference to the bisulphate with a saving of much time which would otherwise be spent in expelling moisture and converting one salt to the other. The sodium salt gives a clearer melt at high temperature than potassium pyrosulphate. According to whether the R_2O_3 percentage is 10, 20, or 30, the 30 g. crucible is filled from one- to three-quarters full of the dry salt. If the salt is quite dry and the fusion is not hurried, the crucible need not be covered, but with the bisulphate or damp pyrosulphate there may be much spattering at first, requiring the use of the crucible lid.**

For melting the salt, the bottom of the crucible is kept about $1\frac{1}{2}$ inches above the top of a $1\frac{1}{2}$ inches high bunsen flame to which only half the usual air supply is admitted. When a perfectly tranquil melt has been obtained, the lid may be removed and the flame very slightly increased. A gradual attack on the residue will be observed: at the same time the molten salt will assume a brown colour if iron is present. After the first half hour the melt gradually emits more and more white fumes of sulphur trioxide, but the

temperature should not be allowed to rise to the point where the melt is hidden by a crust of solid salt until three-quarters of an hour have elapsed. The scum and crust can be broken up by carefully rotating the crucible with the aid of platinum-tipped tongs. By so doing and placing under a strong light, there is usually no difficulty in seeing when the residue of R_2O_3 has all gone into solution. When this is the case it is best to raise the temperature to a low red heat for five minutes to make quite certain that no residue remains unattacked.

The time taken for a fusion varies considerably. It depends not only on the weight of R_2O_3, but also upon the state of subdivision and the ratio of iron to alumina. Thus the R_2O_3 which has been precipitated with the aid of pulp will be attacked much more rapidly than that where pulp has not been used. Whereas a precipitate representing a few per cent. of alumina with scarcely any iron may be completely attacked in fifteen minutes, a precipitate representing 30 per cent. of R_2O_3 and consisting largely of Fe_2O_3 may take a little over one hour. In the author's experience the long time (three to four hours) mentioned by H. S. Washington (p. 182) is not required.

Preparation of Solution.—The melt is deftly swirled round in the crucible as it slowly solidifies and, when practically solid, the crucible is cooled under the tap, care being taken not to allow any water to enter the crucible. In this way the melt is ramified by cracks and the process of solution hastened. The crucible is placed in 200 c.c. of hot water to which 2-3 c.c. of 50 per cent. sulphuric acid have been added, and stirred from time to time while being kept hot on the water-bath. Solution will take twenty minutes to half an hour but, if sulphuric acid has not been added, a precipitate of basic salts is apt to form.

The crucible is removed by means of the glass rod and rinsed inside and out into the solution, which will be distinctly green if much iron is present. If silica has not been thoroughly separated the fact will now be apparent, though the appearance of only two or three small flecks is permissible. There is really no difficulty in discriminating between unattacked residue and silica flecks.

If the silica is appreciable it is to be filtered off, the filter

well washed with hot water, ignited in a platinum crucible, and weighed. A drop or two of 50 per cent. sulphuric acid is added, followed by several c.c. of hydrofluoric acid. The silica is driven off as silicon tetrafluoride, the crucible blasted and re-weighed. The loss of weight represents additional silica. The residue of iron in the crucible is then removed by means of a small-scale pyrosulphate fusion. The melt is dissolved in hot water containing a drop or two of sulphuric acid and added to the main solution. If, as in the majority of cases, the silica has been properly separated in the first place, this further separation will not be necessary.

Removal of Platinum.—Before total iron can be determined, such platinum as has been incorporated by attack on the crucible during fusion must be removed as the sulphide by means of hydrogen sulphide. If this is not done, the platinum sulphide will react with the potassium permanganate, giving a high reading for the titration and a correspondingly high iron value.

The solution is transferred to a 500 c.c. Pyrex wash-bottle fitted with a ground-glass stopper, brought to the boil, and hydrogen sulphide passed for five minutes. The platinum has by this time been precipitated as the black sulphide : it is filtered, and the filter washed three times with water freshly saturated with hydrogen sulphide.

(2) Total Iron and Titania

Determination of Total Iron.—Hydrogen sulphide is then bubbled through the solution for a further fifteen minutes, after which the flask is attached by several feet of rubber tubing to a carbon dioxide cylinder fitted with a good reducing valve. The tubing should be long enough to enable the flask to be transferred from the gas burner to the water tap without discontinuing the supply of carbon dioxide. This gas is bubbled through fairly rapidly at first and the contents of the flask brought to the boil. Once steam is being emitted, the supply of carbon dioxide may be reduced somewhat. Boiling is continued briskly for ten minutes or more, when a piece of filter paper soaked in lead acetate solution is used to test for freedom from sulphuretted hydrogen. A

trace of the gas will cause a black stain or a slight trace a brownish-black stain. The boiling is continued until there has been no trace of hydrogen sulphide for several minutes.

The flask is then stood on wood or uralite by the sink for a minute or two while the excess heat goes off. Then the stream of carbon dioxide is increased again before placing the flask under the tap for cooling. Cooling is most rapidly achieved by imparting a swirling motion to the contents of the flask while it is held under a fast flow of cold water. At the same time the flask is turned over and over so that fresh surfaces are constantly being cooled.

When quite cold, the carbon dioxide is turned off, the tube disconnected, and the flask promptly placed under a 50 c.c. burette filled in readiness with $N/10$ or $N/20$ potassium permanganate. In the course of the titration, care is taken to watch for the first drop of permanganate which causes a pale pink coloration.

Until the worker has successfully made many analyses, he is advised to repeat the reduction of the iron with hydrogen sulphide and the titration with permanganate. The two titrations should not differ by more than a tenth of 1 c.c. If they do, something is radically wrong, and the operation must be repeated until satisfactory agreement is obtained. Sometimes the solution at this stage is cloudy on account of the separation of finely divided sulphur. This must be coagulated by boiling and removed by filtration before the colorimetric determination of titania is commenced.

Titania : General.—Titania gives with hydrogen peroxide a yellow coloration which is utilized for the colorimetric determination of the metal. It has been shown that the depth of colour is increased by the presence of sulphuric acid, and decreased by fluorine, phosphoric acid, and to a lesser extent by high concentration of alkali sulphates.

Most workers find the yellow colour produced by titania and hydrogen peroxide fairly easy to match, though, if anything, it is not quite so simple as the matching of permanganate solutions in the estimation of manganese. The titania yellow is very readily bleached by fluorine, so that if the solution has been obtained by the use of hydrofluoric and sulphuric acids, it is imperative that every trace of the

former acid be removed before the colorimetric comparison is undertaken or a low figure for titania and a correspondingly high one for alumina will result. In spite of its seriousness, this is probably one of the commonest errors in silicate analysis and one which does not show itself in the total. If the iron content of the rock is so high that after oxidation to the ferric state by the permanganate titration the solution is greenish in colour, the colorimetric comparison for titania will be affected. A rather rough-and-ready method of getting over this difficulty is to add, say 2 c.c. phosphoric acid to each solution. It is, however, scarcely possible to measure out the phosphoric acid with sufficient accuracy to insure two equal additions, and it is preferable to add instead an amount of standard ferric sulphate solution to give a weight of ferric iron in the comparison solution equal to that already found in the test solution. In practice, this will not often be necessary.

Colorimetric Comparison : Procedure.—**20 c.c. of a good grade of hydrogen peroxide (20 volumes strength) are added to the test solution, which is then made up to 500 c.c. in a measuring flask by the addition of 5 per cent. sulphuric acid. In those cases where titania is exceptionally low, a volume of 250 c.c. will be better : if titania is high, the volume may have to be made up to 1,000 c.c. If the colour density of the solution is too great to allow of ready comparison after dilution to 1,000 c.c.—***i.e.*,** if more than 3 or 4 per cent. of titania is present—then a gravimetric method will have to be adopted. This situation is more common in the analysis of minerals than in rocks.**

To a second 500 c.c. measuring flask, 20 c.c. of hydrogen peroxide are added, and the volume made up to 500 c.c. by means of 5 per cent. sulphuric acid. Obviously, care must be taken to ascertain that exactly the same volume of hydrogen peroxide is added to both flasks. The contents of the flasks are well mixed and then compared as follows : The comparison is carried out in two Nessler cylinders of exactly the same size and shape, having accurately plane bottoms, and graduated at 50 and 100 c.c. The cylinders should be painted with a thick opaque coat of black enamel, leaving clear only the bottoms and a thin strip down one side of

each. 100 c.c. of the coloured test solution is poured into one Nessler cylinder, and 100 c.c. of the hydrogen peroxide-sulphuric acid solution into the other. A 10 c.c. burette is filled with standard titania solution (see p. 14) which is carefully added little by little to the hydrogen peroxide-sulphuric acid solution until the colour in the two cylinders is accurately matched. After each addition the liquid is stirred and the rod removed before comparison. The final additions of titania solution are made at the rate of one or two drops at a time. The operation is best carried out in daylight before a window, the comparison tubes being held at an inclination of about 45° to a white glazed tile placed between the worker and the window. In this way, provided the narrow non-painted strips are held downward, only transmitted light is used, and the confusing effect of shadows and extraneous reflections is avoided. Colorimetric comparisons, particularly in the case of titania, are not so easily effected in artificial light.

TOTAL IRON AND TITANIA ON A SEPARATE PORTION.—1 to 1.5 g. of the powdered sample are accurately weighed into a 3-inch platinum dish, 15-20 c.c. of 50 per cent. (by weight) sulphuric acid are added and the dish then two-thirds filled with ordinary re-distilled hydrofluoric acid. The dish is heated* (in the fume cupboard) on a sand-bath and occasionally stirred, especially in the earlier stages, until the sulphuric acid fumes strongly and has been so fuming for half an hour. By this time the bulk of liquid will be decidedly less than the volume of 50 per cent. sulphuric acid taken. At about the half-way stage in the evaporation a crystal of potassium nitrate (about the size of a grain of wheat) is added. This oxidises any organic matter or sulphides present, and converts ferrous iron to the ferric state.

The dish is placed on a stone slab or strip of asbestos sheet to cool before water is added to fill it three-quarters full. The evaporation to strong fuming for half an hour is then repeated, but no potassium nitrate is added this time. The

* If an ordinary 6-inch sand-bath is used the flame must be kept quite low, otherwise the acid mixture will get overheated and bump. The mixture is particularly prone to do this when the last of the hydrofluoric acid is being expelled. Should the mixture bump when it is stirred, the operator may sustain serious burns on face or hands.

dish is cooled, water added, and the mixture digested on the water-bath with occasional stirring until all the soluble matter has dissolved. This usually occupies from half to one hour, for anhydrous ferric sulphate dissolves but slowly.

The solution is filtered through a 7 or 9 cm. No. 41 paper and retained, the filter washed with hot water, and then ignited in a small platinum crucible. When all the carbon has been burned off, the uncovered crucible is inclined at about 45°, and just sufficient sodium carbonate is added to give a good fluid melt over a Teclu burner. The melt is kept fused for fifteen minutes and, after cooling and dissolving in dilute sulphuric acid in a white porcelain dish, there must be no trace of black grains. Unless this fusion is thorough, grains of magnetite, ilmenite, tourmaline, rutile, etc., which may have escaped decomposition by the hydrofluoric and sulphuric acids are apt to be incompletely attacked, a correspondingly inaccurate result for ferric iron, titania, and alumina being achieved. If any black grains are observed they are filtered off, the filter ignited, fused with sodium carbonate, and re-dissolved as before. The solution, which is often turbid, is not filtered but added to the previous solution. The combined solution contains all the iron and titania, and is reduced by sulphuretted hydrogen and titrated with standard potassium permanganate as described on page 72, followed by the titania method of p. 74.

When the content of titania is upwards of 3 or 4 per cent., as it may be in some melilite-basalts and many titaniferous minerals, the gravimetric method given below should be adopted.

Gravimetric Method for Titania (see p. 74).—Of the gravimetric methods for titania, Prof. H. F. Harwood informs the author that recent experience with the phenazone method causes him to regard it as very satisfactory and rapid. He decomposes a 1 g. portion of the rock with a mixture of nitric and hydrofluoric acids, carrying out three evaporations to dryness as described under Phosphorus. An ammonia precipitation is carried out, and the precipitate re-dissolved in hydrochloric acid, after which the phenazone method is applied as described by Moser, Neumayer, and Winter (*Monatshifte für Chemie*, 1930, **55**, 85).

(3) Alkalis*

Soda and Potash

General Considerations.—For many years the Lawrence Smith method has been the standard one for the determination of alkalis in insoluble silicates. Though other methods have been suggested recently† which may serve for the more rapid industrial analysis of felspars, with the use of less expensive reagents, they are scarcely suitable for scientific work. For the geologist and petrographer, the accurate determination of the alkalis is a matter of primary importance, and an error here has considerable effect on the calculation of the norm. In the Lawrence Smith method the use of acids in the decomposition is completely avoided. The silicate, or mixture of silicates, is made into an intimate mixture with an equal weight of ammonium chloride and eight times as much calcium carbonate and heated in a platinum or nickel crucible. During the first stage of the heating, the heat is kept only just sufficient to volatilize the ammonium chloride which combines with calcium carbonate to form calcium chloride, ammonium carbonate being expelled. On completion of this stage strong heating is applied which brings about complete decomposition of the silicates. After leaching with water and filtering, the silicates and aluminates of calcium, and the carbonates of iron, calcium, and magnesium are left on the filter while the alkalis pass into solution as chlorides ; excess of calcium also passes into solution. Boron, if present, is for the most part removed as insoluble calcium borate. The rest of the procedure consists of precipitation of the excess of lime by means of ammonium carbonate, expulsion of ammonium salts by heating the evaporated filtrate, removal of the last traces of lime, conversion of traces of alkali sulphate to chloride, weighing of the mixed alkali chlorides, and finally the separation and weighing of the potassium either as the perchlorate or chloroplatinate with the estimation

* On etymological grounds this spelling of the plural is to be preferred to " alkalies " since " kali " in Arabic and Swahili means bitter.

† E. W. Koenig, *Ind. Eng. Chem.*, **7**, 1935, pp. 314-315. " Determination of Alkalis in Felspars. A Modified Hydrofluoric Acid Method."

of soda by difference. On the one hand, great care in manipulation is needed to avoid loss of any of the solution, and, on the other, it is necessary to reduce contamination from glass or porcelain vessels to a minimum by the use of platinum and boro-silicate glass.

It is absolutely essential that a blank determination be made under the standard conditions of working, using a known weight of calcium carbonate and ammonium chloride. Not only do these reagents, particularly the former, contain alkali salts, but the large quantities of distilled water used, and the effect of the ammonium carbonate solution on the glass, all tend to raise the blank. The importance of this blank determination will be realized when it is stated that in the author's experience, using the "A.R." reagents of one of the best London firms, the figure obtained for the "blank" is usually equivalent to between 3 and 5 mg. of alkali chlorides for the usual mixture of 6·4 g. of calcium carbonate and 0·8 g. of ammonium chloride. Taking a particular instance, when the "blank" for the above mixture was 0·0031 g. NaCl and 0·0013 g. for KCl, and the sample taken was the usual 0·8 g., the results obtained before and after the correction for the blank were 3·35 per cent. Na_2O, 2·58 per cent. K_2O, and 3·14 per cent. Na_2O, 2·47 per cent. K_2O. The difference in the total alkalis is here 0·32 per cent. This error would be a serious matter for the geologist, or indeed for most scientific workers.

The alkalis for the "blank" are for the most part held in the calcium carbonate; the ammonium carbonate probably contains the least. Soda always dominates over potash. If the "blank" for the usual mixture mentioned above exceeds 5 or 6 mg. of alkali, it is as well to reject the calcium carbonate. If a pure grade of calcium carbonate is unobtainable, the alkali content can be reduced by repeated washing with boiling water and subsequent drying and re-powdering.

There is no necessity to use the specially shaped platinum crucible recommended for the Lawrence Smith method by some textbooks. Indeed, the complete removal of the sintered cake from such a crucible is much more difficult than from one of ordinary pattern. It is claimed that the

special elongated pattern, when used in an inclined position, permits the use of a higher temperature than any other form of vessel, but if an ordinary platinum crucible is inserted, in an upright position, through a well-fitting hole in a horizontal sheet of asbestos board such as "Uralite," so that only one-third of it projects below into the flame, the most powerful Teclu burner can be used with safety. There is no necessity for the lid to be further cooled by means of a beaker of water or be replaced by a platinum lid in the form of a dish which can be filled with water.

Determination of Blank.—Once the blank has been carefully determined for the supply of calcium carbonate, there is no need for it to be repeated until a new bottle of the reagent is required. It is therefore as well to obtain a supply sufficient to last for a year or two. The contents of the calcium carbonate bottle are thoroughly mixed in the first instance before taking 6·4 g. and mixing with 0·8 g. of ammonium chloride. Thereafter the procedure is exactly the same as is described below for the determination of alkalis with the exception that, after the first stage of gentle heating, the stronger heating for sixty to seventy-five minutes is omitted. Care should be taken to use the same volume of washings and to keep the conditions precisely similar to those generally followed in the determination of alkalis. For this reason it is better to postpone determination of the blank until the beginner has acquired some proficiency and reliability.

Determination of Soda and Potash.—Whenever there is no shortage of the material to be analyzed, the author is in favour of using a 0·8 g. portion for the determination of the alkalis. Only when material is scarce should 0·5 g. be taken, and in that case the quantities of ammonium chloride and calcium carbonate are reduced in proportion.

0·8 g. of the rock or mineral powder is weighed out into a weighed watch-glass, carefully transferred, first by tapping and then by means of a camel-hair brush, into an agate mortar of sufficient capacity (about 4–6 inches internal diameter), and given an extra fine grinding, an operation which takes only a few minutes. An equal weight of A.R. ammonium chloride is then weighed out to the nearest

milligram or two* and added to the powdered sample in the mortar. The two substances are carefully ground together. 6.4 g. of A.R. calcium carbonate are next weighed out to within 2 or 3 milligrams, added to the mortar a gram or so at a time and thoroughly ground together with the other two ingredients. 1 g. of calcium carbonate is retained for cleaning out the mortar. The success of the determination largely depends both on the thoroughness of the grinding of the portion taken and on the degree of mixing achieved. A full quarter of an hour will probably be spent on the mixing after the reagents have been weighed out. The finely mixed powder, which must appear quite homogeneous, is carefully tipped on to a sheet of black cartridge paper which has been kept under the mortar all the time to catch any traces of powder which may have come over the side by accident. The mortar is cleaned out with the remaining 1 g. of calcium carbonate and the assistance of a camel-hair brush. The powder is further mixed on the sheet of paper, and then completely transferred to a platinum crucible with a well-fitting lid, stood on another sheet of black cartridge paper to catch any powder which might otherwise be lost. The operation should be carried out with such care that it is only rarely that a little powder is accidentally spilt : on no account must there be any loss of powder. These operations of weighing, transference, and mixing should be carried out under draught-free conditions.

The crucible, with the lid well fitted, is then placed in a round hole in the sheet of " Uralite " so that about one-third of it projects beneath, and a bunsen burner with a luminous flame about 1-1¼ inches high, protected by a cone upon a star support, is placed so that the top of the flame is about 1-1½ inches below the bottom of the crucible. After a minute or two ammonia fumes can be smelt issuing from the crucible but no white fumes of ammonium chloride must be allowed to escape. If they appear, the flame must be reduced immediately, though the figures given above will be approximately correct for a 35 g. crucible. At the end of twenty to twenty-five minutes ammonia fumes should

* It is preferable to take a milligram or so in excess of 0.8 g. rather than anything less than this amount.

no longer be perceptible and their absence should be confirmed by passing the stopper from the bottle of concentrated hydrochloric acid over the crucible or just to windward of it. If ammonia is still coming off, white fumes will at once appear. This test is much more sensitive than the sense of smell.

When all ammonia fumes have ceased, the crucible lid is removed and held inverted over a flame in order to remove the small amount of ammonium chloride which has sublimed on to it. The lid is replaced and the crucible is heated for sixty to seventy-five minutes over the full heat of a large Teclu burner. When the full heat is applied, there should be only the slightest loss of ammonium chloride for fifteen seconds due to the reagent having sublimed slightly on the upper part of the inside of the crucible. If much ammonium chloride escapes at this stage it is a sure indication that the preliminary heating was insufficient. This check cannot very well be applied if the ammonium chloride on the underside of the lid is not removed first. The preliminary heating takes from twenty to thirty minutes according to the height of flame used and the distance of the top of the flame from the crucible. If the preliminary heating is speeded up so that it takes less than twenty minutes the decomposition will tend to be incomplete, for too much ammonium chloride will be sublimed in the upper part of the crucible and a certain amount will inevitably escape.

For felspars and leucocratic rocks, one hour's strong heating is sufficient but, when large amounts of ferromagnesian minerals are present, it is better to heat for seventy-five minutes. The longer period should be given to amphiboles and pyroxenes and also to micas. The micas are frequently difficult to decompose (see p. 209).

At the end of the strong heating the mixture will have sintered into a hard cake. As soon as the crucible and contents have cooled, they are placed in a 3- or 4-inch platinum dish and leached with hot distilled water on the water-bath for half an hour, the lumps being carefully broken up by means of a moderately thick glass rod. The crucible is well washed out with boiling water. At the end of half an hour the liquid is decanted through a No. 40 11 cm. paper. The

dish is again half filled with boiling water and its contents leached for a further quarter of an hour or so. No lumps must remain. The liquid and sludge contents of the dish are then transferred to the filter and the residue on the paper is washed with boiling distilled water until the volume of the filtrate and washings is 400 c.c.

The residue on the paper is discarded but, before doing so, it is always as well to test for the completeness of the decomposition. The residue is removed by a jet from the wash-bottle into a beaker and dissolved by the addition of strong hydrochloric acid. In a few minutes everything will have dissolved with the exception of flecks of silica. On passing a glass rod round the bottom of the beaker there should be no heavy gritty residue. If there is, the determination must be rejected as the decomposition is incomplete. A few dark grains of iron ore do not matter as these are not decomposed by this method.

A few drops of 1 : 1 ammonia are added to the filtrate which is then heated to boiling. Meanwhile 5-6 g. of A.R. ammonium carbonate have been dissolved in warm water to which has been added about 1 c.c. of ammonia. Half of this solution is carefully added to the boiling filtrate, the other half, kept warm on the water-bath, being reserved for the second precipitation. The liquid is filtered through a 12½ cm. No. 40 paper, and the precipitated calcium carbonate washed three times with hot water. The filtrate is transferred to a platinum dish with a capacity of 600 c.c. (diameter about 7 inches) and placed on a water-bath, preferably heated by electricity. (If a platinum dish of sufficient size is not available, the evaporation has to be done in a porcelain dish but then there will inevitably be some attack on the glaze with introduction of alkalis to the solution. A higher blank results and one which is probably not so constant as when platinum is used). The residue on the filter paper is transferred by means of the wash-bottle to the beaker used for the precipitation and dilute hydrochloric acid is added drop by drop until the residue is just dissolved. The solution is diluted to 300 c.c. and the calcium re-precipitated as before with the ammonium carbonate solution.* The filter paper

* A certain amount of alkali salts is carried down with the first precipitation of calcium and this is recovered by re-precipitation.

used in the first precipitation may be used again for filtering after the second precipitation. The residue is washed once and rejected. The filtrate is added to the first filtrate in the dish, the beaker being rinsed into the evaporating dish. The united filtrates are then evaporated to dryness and left on the water-bath for about half an hour after apparent dryness.

The dish is then covered with a large clock-glass, supported on a silica triangle on a tripod stand, and gently heated over a rose burner so that the flame does not touch the dish and fumes come off only gently. If the fumes are allowed to rush off, they will carry a certain amount of the extremely light and finely divided alkali chlorides with them. The best part of an hour will have to be given to this process with a platinum dish ; longer if a porcelain dish be used. About 25 c.c. of hot water from the wash-bottle are swilled down the sides of the dish so that all soluble salts are brought into solution. A weak solution of barium chloride is added drop by drop, taking note of the precipitation caused by each drop. If the evaporation has been carried out over an electrically heated water-bath, one or two drops usually suffice but, if the water-bath is gas heated, the sulphur fumes picked up will require several drops of barium chloride solution.* (Beginners are apt to add far too much barium chloride at this point. If insufficient ammonium carbonate be added subsequently, the result will be high.) Several drops of weak ammonium oxalate solution are added, followed by a piece of ammonium carbonate, about the size of a grain of wheat, dissolved in several c.c. of water containing a little free ammonia. The contents of the dish are allowed to stand overnight, or at least four hours, in order to precipitate the last traces of calcium.

The dark brown turbid liquid is then filtered through a 7 cm. No. 40 paper into a 3-inch platinum dish, the large dish being rinsed three times, and the paper washed three times. The filter is rejected and the filtrate evaporated to dryness on the water-bath. The dish is covered with a clock-

* Barium chloride is added to convert alkali sulphates present, representing either original sulphur of the sample or that picked up from gas fumes, into alkali chloride by double decomposition. Ammonium oxalate is added to precipitate the last traces of calcium, and ammonium carbonate to precipitate the excess of barium chloride used.

glass and heated over a rose burner to remove the ammonium salts. Meanwhile a 20 g. platinum dish is cleaned, ignited, and weighed. The residue is treated with a few c.c. of hot water, and the solution filtered through a 7 cm. No. 40 paper into the weighed platinum dish, and the filter washed six or seven times with small quantities of hot water. Ten drops of concentrated hydrochloric acid are added and the contents of the dish are evaporated to dryness, the dish being allowed to remain on the water-bath for a quarter of an hour after complete dryness appears to have been attained. The dish is then covered with a watch-glass, placed on a silica triangle, and very cautiously heated by means of a small flame, which is passed to and fro underneath but is not allowed to touch the dish before the expiration of several minutes of such heating. If soda predominates, the alkali chlorides will be very liable to decrepitate ; indeed, absence of any sign of decrepitation indicates that soda is much subordinate to potash. When there is no more risk of decrepitation the dish is heated more directly by the small flame for several minutes, but at a temperature insufficient to melt the alkali chlorides, until the discoloration of the salts due to small amounts of carbon is removed. Stronger heating is then applied until the alkali chlorides just commence to fuse at the edges. The dish is immediately placed in a good desiccator and, after twenty minutes, the contents are weighed as $NaCl+KCl(+LiCl)$.

Dr. M. H. Hey does not discard the residue from the Lawrence Smith fusion, but reserves both it and the calcium carbonate precipitate (which, however, he does not dissolve and re-precipitate). Both precipitates are rinsed back into the platinum dish and evaporated to dryness on the water-bath, then mixed with 0·8 g. of ammonium chloride (no grinding is required) and transferred to the crucible used for the first Lawrence Smith fusion. It is, of course, never possible to achieve a complete transfer but that is unimportant. The mixture is fused again and leached as before, evaporated, and united with the first leachings. With felspars and highly felspathic rocks this second fusion may yield several milligrams of alkali chlorides. This commendable practice does not take much time or trouble and

ensures a good alkali determination in all cases.

It may be remarked that the addition of barium chloride, ammonium oxalate, and ammonium carbonate, all without intermediate filtration, has been severely criticized by C. O. Harvey (*Summary of Progress, Geological Survey Gt. Brit. for* 1936 (1938), Part II, pp. 79-83).

A silica beaker (specially reserved for the purpose) may be used for the filtered leachings. Silica dishes can be used for the operation of leaching, and for the evaporation and expulsion of ammonium salts (provided the temperature in the last-mentioned operation is kept as low as possible). While silica is better than porcelain it is inferior to platinum both from the point of view of contamination and speed of evaporation.

SEPARATION OF POTASSIUM.—The weighed chlorides are dissolved in about 5-10 c.c. of water and a volume of 20 per cent. perchloric acid (not the full strength which is about 60-70 per cent.) is added, equal to ten times the weight of mixed chlorides (*i.e.*, for 0·07 g. of chlorides, 0·7 c.c. of the dilute acid). The dish is placed on the water-bath and the liquid evaporated to a very small bulk, when white fumes of perchloric acid appear. The dish is then transferred to an asbestos covered gauze and cautiously heated over a very small flame until dense white fumes of the acid have rolled off for a minute or two. A few c.c. of water are added, and the evaporation and heating to fuming repeated, the final heating being continued until the salts are nearly dry. In this way, complete conversion of the chlorides to perchlorates is assured.

A few c.c. of the alcoholic wash liquid No. 1 (see p. 11) are added and the crystals of perchlorate are broken up with a small stirring rod, $2\frac{1}{2}$-3 inches long, specially prepared for this and other small scale operations in the determination of alkalis. The crystals are then filtered through either a Munroe platinum crucible* or a fritted glass filter-crucible, using a suction pump (see p. 42). Whichever type is used, the filter crucible should have been dried in an oven at 110° C.

* A Munroe crucible keeps a very constant weight, which cannot be said of the glass filter. Moreover, the Munroe allows of much more rapid filtration with no passing of fine perchlorate crystals.

for three-quarters of an hour, cooled in a desiccator, and weighed before use. If a glass filter is used, it must be a fine one such as a Jena No. 4. Coarser filters, though much faster, are apt to allow some of the finest crystals of potassium perchlorate to pass through. The transference of the crystals from the dish to the filter is effected with wash liquid No. 2. The perchlorate crystals tend, however, to adhere to the bottom of the platinum dish which needs to be rubbed round a number of times with the glass rod until further washing shows it to be clean. This can be ascertained by rubbing the bottom and then holding the dish sideways while a little wash liquid is played on it from a wash-bottle. The heavy crystals of potassium perchlorate then collect at the bottom of the liquid. Two or three small crops of potassium perchlorate may be obtained in this way after the dish appears to be clean. This effect is of course much more pronounced in a scratched dish than in a newly blocked one. The potassium salt in the crucible is then thoroughly washed with wash liquid No. 2 from a small wash-bottle specially kept for the purpose. The filter crucible is placed in a small crucible stand, dried in an air oven at 140° C. for an hour, and weighed. From the weight of $KClO_4$ the equivalent of KCl is calculated and the weight of NaCl found by difference.

Test for Lithia

Lithium perchlorate, like the sodium salt, is soluble in the alcoholic wash liquids, so that its presence may be tested for spectroscopically in the filtrate and washings from the potash salt without any effect on the alkali determinations.

A very small pinch of A.R. sodium carbonate is added to neutralize the perchloric acid and the liquid is evaporated to a small bulk, when a drop or two of concentrated hydrochloric acid is added and the flame test carried out. A small pocket spectroscope and a bunsen flame are most suitable for this test, for when an arc with electrodes of stout copper wire is used lithia is observed nearly every time but only very markedly when it is present in more than spectroscopic traces.

Other Methods

G. G. Marvin and L. B. Woolaver have published (*Ind. Eng. Chem., Anal. Edn.*, 1945, **17**, 554-556) what is claimed to be an improved method for the determination of sodium and potassium in silicates. These authors maintain that the principal difficulty encountered in the J. Lawrence Smith method is the necessity for grinding an already weighed sample, and keeping such a procedure strictly quantitative. While the present author considers this difficulty to be exaggerated — it is not open to appreciable error provided a 0·8 gm. sample is taken, a sufficiently large and unscratched agate pestle and mortar is used, and the precautions mentioned on pp. 79-80 are carefully observed — Marvin and Woolaver have indeed introduced a novel way of obtaining the alkalis in solution and removing magnesium, iron, and aluminium. They decompose the sample with a mixture of hydrofluoric and perchloric acids, removing excess hydrofluoric acid by fuming in the usual way. On thermal decomposition of the perchlorates so obtained, the perchlorates of sodium, potassium, and calcium give the corresponding chlorides and evolution of oxygen, whereas the perchlorates of magnesium, iron, and aluminium are hydrolyzed by the water of hydration contained in the molecule to yield perchloric acid, water, and the corresponding oxide (*Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 474). By leaching the decomposed perchlorates with hot water made slightly alkaline with ammonium hydroxide (to repress the solubility of magnesium oxide), a solution is obtained containing essentially only sodium, potassium, and calcium chlorides. Only the removal of calcium and ammonium salts from this solution is required to obtain a solution to which the usual perchlorate method of alkali separation can be applied. While this method appears to give good results for felspars, and glasses, it unfortunately fails if phosphates or sulphates are present. It is therefore applicable to only a very limited range of silicates and should not be applied to any rocks.

In cases where, as in orthoclase, the proportion of potash to soda is extremely high, it is better to determine soda as

sodium zinc uranyl acetate, and to get potash by difference.

(4) Ferrous Oxide

General.—Ferrous oxide is usually the simplest and quickest determination in silicate analysis. The powdered material is decomposed in a crucible with a well-fitting lid by a boiling mixture of sulphuric and hydrofluoric acids, the escaping steam excluding the air, and the liquid at once titrated with permanganate. This simple arrangement has been proved to be thoroughly efficient, and on account of the short time taken (three to five minutes), more complicated arrangements to exclude the air are unnecessary.

It has been shown that manganic fluoride in dilute solution is scarcely dissociated at all. The manganic ion, in this case, passes as fast as it is formed into the undissociated state or into a complex ion so that, in the presence of hydrofluoric acid, bivalent manganese is readily oxidized by permanganate. As a result, there can be no sharp end-point in the titration of ferrous iron in the presence of much hydrofluoric acid. What happens is that the pink colour soon disappears, and this the more rapidly the greater the amount of hydrofluoric acid or of manganous salt developed as the result of reduction of the permanganate solution added. This difficulty is readily overcome by the addition of boric acid which, by forming the complex fluorboric acid, renders the hydrofluoric acid inoperative.

Some silicate minerals such as garnets, staurolite, etc. which are rather difficult to decompose by a mixture of hydrofluoric and sulphuric acids, need to be very finely ground. Should the decomposition still be incomplete, the liquid, after titration, is filtered, the residue dried, and the decomposition and titration repeated. With a few refractory minerals such as tourmaline and lusakite* this process repeated several times is the only way to obtain an approximation to the FeO content, unless a pressure tube constructed entirely of platinum is available. In such cases the methods of p. 181 should be used.

In the case of rocks and of those minerals which are not

* A. C. Skerl and F. A. Bannister, *Mineralog. Mag.*, 1934, **23**, 598-606.

difficult to decompose with a mixture of sulphuric and hydrofluoric acids, it is inadvisable to powder the material beyond, say 90 mesh, for it has been shown that prolonged grinding tends to oxidize some of the ferrous iron in silicate minerals.* Should very fine grinding be essential, it is best to do this under absolute alcohol which is afterwards allowed to evaporate without the application of heat.

When carbonaceous matter is present in a rock, as in carbonaceous shale or clay, it is oxidized by the permanganate so that a high figure for FeO results. FeO determinations on such rocks can at best be regarded as approximate, and a note to this effect should be appended to the analysis. Graphite does not affect the FeO determination.

Although pyrite is unattacked by a mixture of hydrofluoric and sulphuric acids, there is some oxidation of the pyrite when ferric salts are present, as was by shown by H. N. Stokes.† This results in a lowering of the FeO figure and raising that for Fe_2O_3, but for the amounts of pyrite found in most rocks the effect is negligible. Nevertheless, a considerable error would result in the case of a rock high in ferric iron and containing much pyrite. The extent of the attack on the pyrite would depend on the fineness of the powder, and on this too would depend the amount of oxidation during grinding, so that correction is not a simple matter.

Trivalent vanadium is oxidized by permanganate to the pentavalent state, so that the presence of trivalent vanadium leads to high results for ferrous iron. If, therefore, V_2O_3 has been determined and is appreciable (say 0·05 per cent. or more), as it may well be in many basic rocks, a correction should be applied on the basis of one molecule of V_2O_3 (149.9) in oxidizing to V_2O_5 requires as much oxygen as four molecules of FeO (287.4) when oxidized to Fe_2O_3. The figure (x) to be deduced from the uncorrected value for FeO is therefore given by the proportion 149·9 : 287·4 : : V_2O_3 present : x. The example given by Hillebrand-Lundell (p. 780) where, in a rock containing 0·13 per cent. V_2O_3, failure to correct for vanadium would have made the per-

* W. F. Hillebrand, *J. Am. Chem. Soc.*, 1908, **30**, 1120.
† *Bull. U.S. Geol. Survey* 186 (1901); *Am. J. Sci.*, 1901, **12**, 414.

centage figures for FeO and Fe_2O_3 respectively 2·50 and 2·22 instead of 2·25 and 2·36, is rather extreme but may occur nevertheless among the more basic rocks.

Another constituent which, in exceptional cases, may affect the determination of ferrous iron is manganese dioxide, usually in the form of pyrolusite. If manganese dioxide is present, the amount of ferrous oxide has to be correspondingly increased and the ferric oxide decreased. If, however, the ferrous oxide exceeds the manganese dioxide, the proportion of the latter cannot be determined and the necessary correction cannot be made. These situations will be encountered only in the analysis of manganese ores, highly manganiferous phyllites, gondites, khondalites, etc.

If ferrous iron and Mn_2O_3 or MnO_2 occur together (which, except in the case of partially decomposed manganese silicate minerals, is probably most uncommon), it is impossible to determine either. In strict point of fact, it is really impossible to determine FeO or Mn_2O_3, or MnO_2 in most rocks and minerals; all that the chemist really does is to determine the *net state of oxidation*. At the same time he has to assume that V is present as V_2O_3, Ce as Ce_2O_3, etc., and Fe partly as FeO and partly as Fe_2O_3; or else that V is present as V_2O_5, Fe wholly as Fe_2O_3, and Mn partly as MnO and partly as Mn_2O_3, or partly as Mn_2O_3 and partly as MnO_2.

PROCEDURE.—**0·8 g. of the sample is weighed into a 35 g. platinum crucible with a well-fitting lid. A retort stand with silica triangle and a bunsen burner are prepared in the fume cupboard, which should be illuminated. A supply of distilled water is boiled in a 2 litre flask fitted with an inlet tube reaching to the bottom and a short exit tube, the water is almost saturated with boric acid, boiled until air-free, the flask then connected with a cylinder of carbon dioxide, and cooled under the water tap in an atmosphere of carbon dioxide. For all but the most accurate work, however, if a still is constantly working, it suffices to take some of the freshly distilled water and saturate it with boric acid powder immediately before use.**

About 200 c.c. of this solution is placed in a 600 c.c. beaker and a stirring rod introduced. A 50 c.c. burette is filled in

readiness with $N/20$ potassium permanganate and a white porcelain tile is placed on the burette stand. The platinum-tipped crucible tongs, a watch, and the beaker are placed alongside the retort stand in the fume cupboard.

A few drops of water from a wash-bottle are directed on the side of the crucible so that its contents are moistened without "dusting." 8 c.c. of 50 per cent. sulphuric acid are added and then an equal volume of "re-distilled" hydrofluoric acid. Without delay, the closed crucible is heated with the full bunsen flame which is deftly passed to and fro underneath but barely touching the crucible. In about three or four minutes the contents will commence to boil. Great care must be taken to note the first escape of steam and then to moderate the heat applied so that gentle boiling is maintained. The object is to keep a small jet of steam escaping so that the air is displaced. The boiling is continued for three minutes when, without delay, the crucible, lid, and contents are plunged into the boric acid solution and immediately titrated with the permanganate. The glass rod may be used, if necessary, to remove the crucible lid under the boric acid solution, and the whole is then continuously stirred during titration. The coloration at the end point should last at least thirty seconds but will fade on standing on account of free hydrofluoric acid. This determination, which can be done in less than half an hour, should be repeated. Unless spurting has taken place, there is usually no difficulty in obtaining concordant results.

DETERMINATION OF FERROUS IRON IN REFRACTORY SILICATES.—The standard method for ferrous oxide described above fails in those cases when the material under analysis consists of or contains ferrous minerals not readily decomposed by a mixture of hydrofluoric and sulphuric acids. For the treatment of these cases see p. 181 in Chapter VII, "Special Methods".

ALTERNATIVE METHOD FOR FERROUS IRON.—Reference is made in Chapter VII (a), Section 7 (p. 186), to the use by Dr. M. H. Hey of iodine monochloride solution in hydrochloric acid for the estimation of ferrous iron in a sodium metafluoborate melt, the liberated iodine being titrated with potassium iodate. In his original paper

describing this method (*Mineralog. Mag.*, 1941, **26**, 116-118) Hey suggested that it could be applied directly to the determination of FeO in olivine and other minerals soluble in cold strong hydrochloric or hydrochloric and hydrofluoric acids. He has since developed this into a general method for the determination of FeO* in rocks and minerals. He finds that solution in a mixture of hydrofluoric acid, concentrated hydrochloric acid, and iodine monochloride, at room temperature, and titration of the iodine liberated by potassium iodate, provides a simple and very accurate method for determining FeO in all rocks and minerals that dissolve completely in this mixture; and, fortunately, it seems that most minerals that are attacked by hot dilute sulphuric acid and hydrofluoric acid dissolve completely in this solvent. Thus obsidian is dissolved in 30-60 seconds, and plagioclase in 1-2 minutes.

The reactions involved are :—

$$\begin{cases} 2ICl + 2Fe^{\cdot\cdot} \rightarrow I_2 + 2Cl' + 2Fe^{\cdot\cdot\cdot} \\ 2I_2 + KIO_3 + 6HCl \rightarrow KCl + 5ICl + 3H_2O \end{cases}$$

Giving a net overall reaction of :—

$$4Fe^{\cdot\cdot} + KIO_3 + 6HCl \rightarrow KCl + ICl + 3H_2O + 4Cl' + 4Fe^{\cdot\cdot\cdot}$$

The obvious advantage of this method is that, iodine being liberated as fast as ferrous iron passes into solution, and the solution being quite stable to air, both before and after titration, the danger of oxidation of ferrous iron is eliminated. The method is thus most valuable when there is very little FeO present, or when the ratio of FeO : Fe_2O_3 is very large or very small. The doubts about air-oxidation that must always arise with the Pratt method, especially in cases such as these, can be set at rest by employment of Hey's method. Caution, however, should be observed if pyrite is present. Hey reports that he has not yet investigated the behaviour of pyrite fully, but that the attack of the mixture on pyrite is certainly not marked.

The method has the following further advantages : (1) The carbon tetrachloride-iodine end-point employed is one of the most sensitive in all volumetric work. (2) If the end-point is overshot, a stable solution for convenient

* "Analytical notes II. The 'ferrous iron' and silica determinations in rocks and minerals." Read to Minerological Society, June 23rd, 1949.

back titration is available in potassium iodide. (3) If material is short, the titrated solution can be evaporated and used for the determination of other constituents by the scheme of pages 193-194, with the added advantages that, no foreign metal other than potassium having been added, manganese can be determined, and there is no boric acid to be removed.

*PROCEDURE.—**1 g. of the powdered rock or mineral is weighed into a large platinum crucible or a small platinum dish, and an excess of 0·4 M ICl solution in concentrated hydrochloric acid† (according to the percentage of FeO expected) is added, together with enough concentrated hydrochloric acid to bring the bulk to 20 c.c. The mixture is stirred with a platinum rod and 10 c.c. of 40 per cent. A.R. hydrofluoric acid added. The mixture is stirred and allowed to stand, with occasional stirring, until the powder is dissolved. If solution is slow, the crucible should be covered with its lid and put aside under a small wax-lined bell-jar.**

The solution is titrated with M/40 (*N*/10) potassium iodate from a weight burette (weighed to 0.001 g.), using carbon tetrachloride as indicator, with vigorous stirring, and back titrated with *N*/100 potassium iodide to the first violet tint of the carbon tetrachloride. This should not be regarded as the final result; the solution should instead be set aside under a waxed bell-jar for some hours. In the majority of cases there is no further liberation of iodine, but, if there is, it is usually due to small amounts of resistant minerals slowly dissolving. The solution, therefore, is allowed to stand until the amount of free iodine, if any, ceases to increase, when, if necessary, a further titration is made. The solution is quite stable to air, both before and after titration.

* The author is indebted to Dr. Hey for kindly supplying details of his method prior to their appearance in the Mineralogical Magazine.

† Prepared by dissolving 10 g. of KI and 6·44 g. of KIO_3 in 25 c.c. of water and 75 c.c. of conc. HCl. A little pure CCl_4 is added to the bottle, and, after shaking, the CCl_4 should be a very pale violet. If it is colourless, add dilute KI, drop by drop, till a trace of free iodine is present, while, if the CCl_4 is distinctly coloured, add dilute KIO_3 till it is almost decolorized after shaking. 1 c.c. of 0·4M ICl is needed for each 3 per cent. of FeO expected, plus a small excess. For minerals almost free from FeO, a weaker ICl solution is appropriate.

It should be noted that the titrated solution must contain at least one-third of its bulk of concentrated hydrochloric acid. Very small percentages of FeO (0·1 per cent. or less) can be confidently determined; neither is there danger of loss of FeO by oxidation in FeO-rich rocks. If desired, the liberated iodine may be re-oxidized by additions of potassium iodate while the rock is still dissolving, instead of waiting till solution is complete.

If when the carbon tetrachloride is added to the reaction mixture it shows no trace of iodine, this is an indication *that the rock is in a peroxidized condition.* In this case titrate with $N/10$ (or weaker) KI and report as "available oxygen." If there is much available oxygen, there is some slight risk of loss, and a fresh determination should be undertaken in which a known excess of potassium iodide is added at the start*. This method is satisfactory for rocks bearing manganese dioxide.

(5) Hygroscopic Moisture

General.—The amount of hygroscopic moisture found will depend on (*a*) the degree of fineness to which the sample has been powdered, and (*b*) on the humidity of the atmosphere at the time of crushing and placing in a specimen tube. The temperature at which the drying is carried out is usually 110° C., though some workers have used 105° C. Whichever temperature is used should be stated. The difference between the total amount of water in the rock and the hygroscopic moisture is taken as representing the water held in chemical combination. It is matter of considerable importance that the hygroscopic moisture should be determined in addition to the total water, for the former is generally a measure, together with carbon dioxide, of the freshness of the rock (see, however, p. 28).

Procedure.—**The determination of hygroscopic moisture is very simple and one which can take care of itself while other manipulations are in progress. A thin watch glass**

* The "available oxygen" liberates chlorine which is held as ICl_3; but since ICl_3 is not so stable in air as ICl or iodine solution, it is preferable to add a known excess of potassium iodide.

which conveniently fits the balance pan and weighs about 10-20 g. is carefully weighed. 2 g. of the powdered sample are evenly spread over the centre of the watch glass, and the whole weighed again. The watch glass is then placed in an air-oven, heated either by gas or electricity at 110° C., for at least two hours, though a longer period will do no harm. At the end of this time the watch glass is placed in a desiccator, cooled, and weighed, the loss in weight representing the content of hygroscopic moisture.

Special care should be taken by carrying the watch glass in a desiccator to obviate possible loss of powder from draughts. Moreover, to prevent the possibility of anything in the nature of rust or scale falling from the top of the inside of the oven into the watch glass, a sheet of glass on a support made of stout glass rod is interposed. If a gas burner is used, it should be a bunsen fitted with a rose burner. Even with gas heating it is an easy matter to keep the temperature of the oven between 108° and 112° C., provided there are no draughts: greater variation than this, particularly on the high side, should be avoided.

(6) Combined Water

General.—The difference between the hygroscopic moisture given off at 110° C. and the total water found is taken as representing an approximate measure of the combined water and is expressed as $H_2O+110°$ C.

Contrary to a widespread belief, even among geologists, it is not always a simple matter to drive off all the combined water of a rock or mineral, as reference to pp. 269-274 of Chapter XI. will show. In the past, the Penfield method has been widely used and is still advocated in the fourth edition of Washington. In this method the rock powder is ignited in a tube of hard glass, closed at one end, and having a bulb blown in the middle. The heated end containing the powder is pulled off, the portion with the expelled water is weighed, and this portion again weighed after thorough drying. There can be no question that the method is sound, provided that the material under test will give off all its combined water in a quarter of an hour

or twenty minutes at a temperature which the glass will withstand. But not only do many rock-forming minerals refuse to part with more than a fraction of their combined water until excessively high temperatures are reached (800°-900° C.) which the glass will not withstand for long, they require considerably more than a quarter of an hour to drive off all the water. Some or all of the amphiboles, micas, kaolin group, talc, staurolite, topaz, and chondrodite require temperatures of 900° C. or over for one hour before the water is completely given off. The last four minerals mentioned require a temperature of well over 1,000° C. Recent work in which the writer participated has revealed the surprising fact that such commonly occurring rock-forming minerals as the epidotes give off only a negligible part of their combined water when heated at a temperature of 900-1,000° C. in a current of dried air for one, two, or even three hours.* It is clear, therefore, that the Penfield method is unsuited to the majority of rocks, though it is permissible in the case of fresh basalts and dolerites containing only pyroxenes, felspars, and perhaps quartz. But even in the case of felspar, where the water is non-essential, it has been shown that most of the water is given off between 800 and 900° C.† As our data on the dehydration of rock-forming minerals increases it becomes abundantly clear that the best all-round method is one in which the material contained in a silica boat is heated in a current of dried air inside a silica tube for one hour at a temperature of about 1,000° C. This method is described first and suitable modifications for the few cases in which it fails are also given.

A method which cannot be too strongly condemned is that of "loss on ignition." It consists of noting the loss of weight when one gram or so of the powdered material is strongly ignited in a platinum crucible. The water may be driven off, but so too will the carbon dioxide of carbonates, sulphur of sulphides, sulphuric anhydride of sulphates, and any carbon or hydrocarbon. Micas and amphiboles may lose

* "Anomalies in the Analytical Determination of Water in Epidote," by A. F. Smethurst, *Mineralog. Mag.*, 1935, **24**, 173-179.

† G. R. Skelton and H. H. Holscher, *Bureau of Standards Research Paper*, 420, 356 (1932).

fluorine. These factors will tend to give a high result. The oxidation of ferrous iron, which is bound to occur, will tend to give a low result. The result of "loss on ignition" is therefore the algebraic sum of these opposing factors. Attempts to correct for the oxidation of ferrous iron are worthless since complete oxidation is never accomplished. It follows that the "loss on ignition" method will give an accurate result only in the rare case where ferrous iron is absent and there are no volatiles other than water to be driven off on heating. The only excuse for adopting this method is the absence of better facilities, and the words "loss on ignition" must be returned with the analysis.

PROCEDURE.—**The apparatus shown in Fig. 7 consists of a "Vitreosil" tube 18 inches long, having a 3-inch length of transparent fused silica let into the middle, set in a gas furnace. Pieces of "Uralite" sheet, suitably cut, are placed near each end to protect the rubber bungs from becoming overheated. At one end the tube is connected to a weighed calcium chloride tube followed by a calcium chloride guard tube, a gas-washer acting as safety bottle, and a suction pump wired on to the water tap. At the other end the air aspirated through the apparatus passes first through a small U-tube containing a plug of cotton-wool to remove dust, then through a small bubbler containing phosphoric acid to indicate the speed of the air current, and then through a drying apparatus before entering the silica tube. The drying tube may be simply a length of 18 inches or so of broad glass tubing packed with calcium chloride or the tube may be doubled back on itself to give the more compact form shown in Fig 8. There must be no space over the top of the calcium chloride which must be closely packed, the granules becoming finer as the silica tube is approached. The calcium chloride used in the weighed absorption tube should have been previously saturated with carbon dioxide by placing in a gas tower attached to a carbon dioxide cylinder. The suction pump is worked full pressure, but by means of two screw clips inserted in the rubber tubing between the pump and the safety bottle, the bottle and the weighed calcium chloride tube respectively, the current of air is adjusted to one to two bubbles a second. During the**

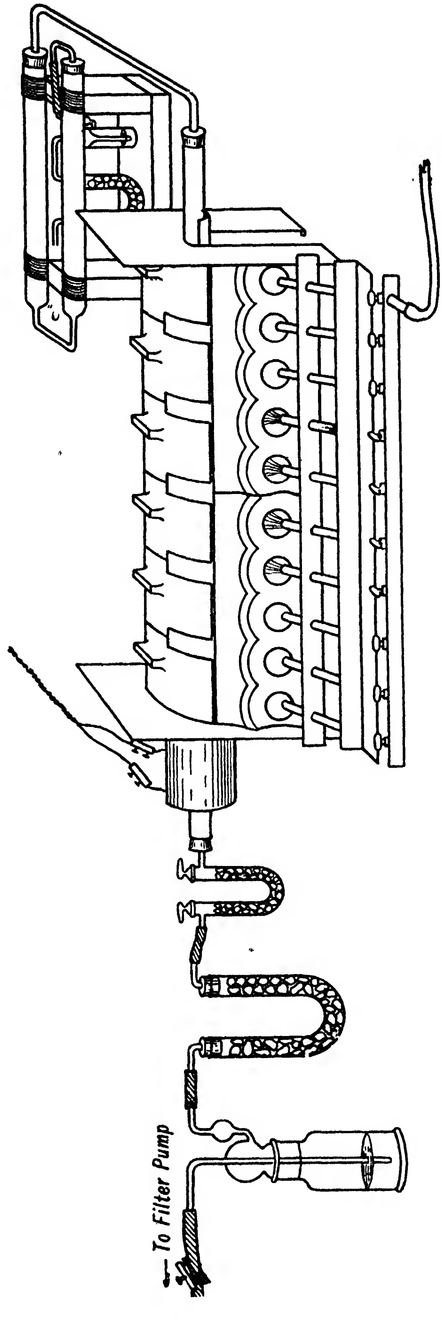


FIG. 7.—APPARATUS FOR DETERMINATION OF TOTAL WATER.

course of adjustments such as this, and when the apparatus is not in use, an empty U-tube is fitted in the place of the weighed one. That part of the silica tube between the end of the furnace and the weighed U-tube should be kept warm by being wrapped in asbestos, or better, it is surrounded by a coil of nichrome wire set in a mixture of asbestos wool and special cement so that the temperature is maintained at 60° C.

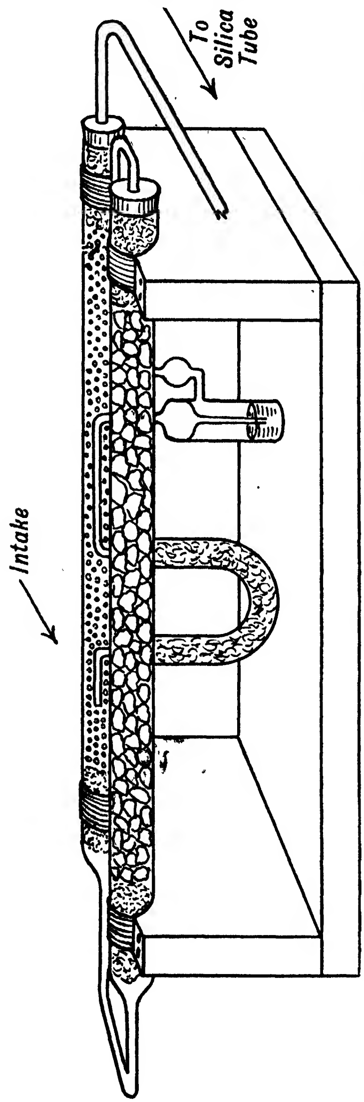


FIG. 8.—ENLARGED VIEW OF COMPACT FORM OF DRYING TUBES USED IN THE APPARATUS OF FIG. 7.

The air current having been adjusted, the furnace is lit and the tube heated to bright redness for three-quarters of an hour. The tube is then allowed to cool with the air still passing through it. Meanwhile a silica boat has been ignited and weighed, and the sample weighed into it. The boat may be conveniently carried, and at the same time protected from draughts, by placing it in a desiccator jar in which there is no desiccant. The calcium chloride tube which has been standing in the balance case for at least thirty minutes is weighed by being suspended from the hook by copper wire, and is carried in a beaker.

When the silica tube is cool, the weighed absorption tube is fitted in place of the empty one, and the boat is pushed

along inside the combustion tube from the other end by means of a length of copper wire with a crook until it reaches the transparent section. The rubber bungs are inserted without any loss of time. A final test is made for freedom from leaks, after which the furnace is lit, and at the end of ten minutes is increased to its full heat. Heating must not be carried on too near the bungs and, with a tube 18 inches long, the use of four or five burners will be sufficient. The furnace, if working well, should attain a temperature of nearly 1,000° C. in the second half-hour.

At the end of forty-five minutes' heating, the side tube leading into the weighed U-tube (which must always be inserted directly into the rubber bung of the silica tube so that its end is flush with the inner surface of the bung) is examined. If there is moisture present in this, it is carefully driven into the main part of the tube by holding a hot tile from the furnace nearby, so that radiant heat falls upon it. Care must be taken not to overheat the rubber bung or sulphur will pass into the inlet arm of the U-tube. The inlet arm having been dried, it is examined again five minutes later. If it has become at all steamy it will indicate that water is still being given off. The side tube is again cleared of moisture by means of the hot tile. Heating should not be stopped until there has been no trace of moisture shown in the inlet tube for ten to fifteen minutes. This usually takes one hour but, in the case of rocks rich in mica, seventy-five minutes are frequently necessary. The apparatus needs no supervision beyond a glance now and again to see that the rate of bubbling is remaining steady : if this is variable it usually indicates a leakage, but it is a simple matter to test for leaks when, as in this case, there is a bubbler at each end of the apparatus.

When the furnace is extinguished, the taps on the U-tube are closed, the tube is replaced by the dummy one, and is then stood in a beaker in the balance case to cool before weighing. The bung is not weighed.

As soon as the dummy tube is placed in position, its taps are opened, tiles are removed from the furnace, and the silica tube is allowed to cool with the current of dried air passing through it. After thirty minutes, the stopcock on the outlet side of the calcium chloride tube is opened momentarily

to equalize the pressure, after which it is weighed. The increase in weight represents the total water content of the material under test plus a small blank for the apparatus. The blank is determined immediately, or if the humidity is steady during the day, then sometime during that day. Thus it is possible in one full day to make three determinations and to do one blank. The blank is determined by replacing the weighed calcium chloride tube into the apparatus and heating for the same time as the other determinations. With an efficient drying train the blank for one hour's run will usually be about 0·0007 g. to commence with, rising after some months to perhaps as much as 0·002 g., when the calcium chloride should be renewed. In the author's experience in London the average blank for this apparatus is something very close to 1 mg. per hour, so that, with a 2 g. sample, neglect of the blank would give a result 0·05 per cent. high.

PRESENCE OF VOLATILES.—If the material under examination contains volatile substances (other than carbon dioxide), it is necessary to use a retainer to prevent them coming into the calcium chloride tube and giving a high result. If sulphates are present sulphur trioxide will be evolved (as from alunite); if sulphides are present sulphur dioxide will be evolved; some micas, and amphiboles rich in fluorine, may give off sufficient of this gas to attack the silica tube. A cover of freshly ignited quicklime (ignited for twenty minutes in a platinum dish over a Teclu burner and stored in a desiccator) will form an efficient retainer. If sulphur is given off, as from a rock containing native sulphur, granules of pure silver packed in the cool part of the silica tube between the boat and the U-tube will prove an efficient retainer. Copper can be used but, if it gets heated, there will be some breaking-down of the water to hydrogen and oxygen, which does not happen with silver.

REFRACTORY MINERALS.—In the case of the minerals talc, epidote, staurolite, phlogopite, topaz, chondrodite, and hydroxyapatite (and other members of the apatite group containing OH), or rocks containing an appreciable amount of these minerals, the method described will give a low result or fail almost entirely, due to insufficient tem-

perature. For these the method is modified as follows : The silica tube is replaced by one of special combustion glass, and the silica boat is replaced by one made of platinum. ½-1 g. of the mineral is mixed with as much anhydrous sodium tungstate (dried by heating for half an hour, with frequent turning over, in a porcelain dish at a temperature well below the melting point of 795° C.) as the boat will conveniently hold. The furnace need not be run at its full heat, for as soon as 800° C. is reached the sodium tungstate fuses and decomposes the material. The process can be watched by removing a tile from time to time. The melt should be kept in a well-fused condition for thirty minutes, making the time for the whole of the heating about forty to forty-five minutes.

In special cases, other fluxes, such as sodium carbonate, or sodium metafluoborate, may be preferable ; the flux must in all cases be carefully dehydrated.

Blank for Special Method.—If quicklime is used as a retainer or sodium tungstate is used for decomposition, a batch of dried material is prepared and stored in a desiccator. The blank is then carried out on a weighed amount of the reagent. In the actual determinations the amount of the reagent used should be roughly weighed as speedily as possible and the blank adjusted proportionately.

Alternative Apparatus.—C. O. Harvey, in an endeavour to combine the simplicity and compactness of the Penfield method with the greater adequacy of the silica combustion tube method, has devised an alternative apparatus* which, in straightforward cases where the rock is known to be substantially free from volatile constituents other than water and carbon dioxide and so no special retainer is required, may take the place of the apparatus of Figs. 7 and 8. That apparatus, however, remains the only standard apparatus applicable (with suitable retainers) to all cases. Harvey's apparatus has the slight advantage of requiring little space and no water suction pump, but achieves this at the expense of its range of applicability.

Harvey's apparatus consists of a silica test tube, supported at its upper end, in a position slightly inclined from

* *Bull, Geol. Survey Gt. Britain,* No. 1, 1939, pp. 8-12.

the horizontal, by passing through a sheet of asbestos composition which also acts as a heat screen to the absorption end. The upper, open end of the silica test tube carries a rubber stopper on to which fits an ordinary weighing bottle containing a heap of 4 or 5 g. of calcium chloride (previously saturated with carbon dioxide). A second, tiny borehole through the rubber stopper carries a fine jet made of capillary tubing, the drawn out part extending practically to what is normally the base of the weighing bottle. On passing outside the rubber stopper, the jet is bent vertically at right angles and passes at once into an inch or so of the full gauge capillary from which the jet has been drawn. To this in turn is fitted a short calcium chloride tube ending in a bulb and a small external aperture, which removes the water from the air drawn into the apparatus during cooling. The material under examination is contained in a platinum boat resting in the lower end of the silica test tube, which is heated by means of either an ordinary or a blast Méker burner.

The apparatus is gradually raised to the fullest heat attainable, and thus maintained for at least half an hour, in order to condition it. On cooling, a blank is determined in the following manner. The weighing bottle is removed, quickly stoppered, weighed, and restored to its position on the apparatus. The temperature is gradually raised to the full over a period of about thirty minutes, and maintained at the full for ninety minutes. After cooling for thirty minutes, the weighing bottle is again removed, stoppered with the same stopper and weighed.

For the actual determination, about 2 g. of material are weighed into the platinum boat and the same procedure repeated as for the blank. The weighing bottle should always be stood in the balance case for fifteen minutes before weighing, the silica test tube being kept closed meanwhile by means of a similar, but empty, weighing bottle. When not in use, the apparatus is left connected to the weighing bottle containing calcium chloride.

Estimation of Traces of Water.—A procedure which is claimed to be particularly suitable for the estimation of

traces of water is E. Dittler and H. Hueber's modification* of J. Lindner's method. The water is caused to react with α-naphthyl phospho-chloride at 100° C. with production of hydrochloric acid, which is then absorbed in baryta water and determined volumetrically.

(7) Manganese and Baria

General.—By means of the colorimetric method described below, manganese can be determined with great accuracy for the quantities which normally occur in rocks. For amounts of MnO in excess of about 1 per cent. it is better that the manganese be determined in the main portion as described in Section 6 of Chapter VIIA. The method given for barium leads to highly accurate results.

Procedure.—**2 g. of powdered material are accurately weighed into a 3-inch platinum dish, 15 c.c. of 50 per cent. (by weight) sulphuric acid are added, and about 25 c.c. of hydrofluoric acid ("re-distilled"). The mixture is stirred with a platinum stirring rod. If there is much carbonate present the fact will be obvious at this stage. After a little heating, pyrite, graphite, and carbon also become obvious. The contents of the dish are then evaporated twice to strong fuming as described under "total iron" on p. 75, taking care midway through the first evaporation to add a small crystal of potassium nitrate. The final residue, after cooling, is digested with water on the water-bath for ten minutes when, if barium is to be determined, it is filtered through a double 40 11 cm. paper and particularly well washed with hot water. If baria is not be determined, a much more rapid filtration will be obtained by the use of a single No. 41 paper and only a few washings. The residue on the double 40 paper contains all the barium as sulphate, in addition to other substances: it is kept for the baria determination.**

Manganese Colorimetrically.—**To the filtrate from above is added just sufficient phosphoric acid to decolorize the iron salts present. 0·1-0·3 g. of potassium or sodium periodate is added and the solution heated to boiling point. The colour of permanganate usually appears before the liquid**

* *Zeits. Anorg. Chem.*, 1931, **195**, 41-59, and 1931, **199**, 17-27.

boils, but, if not, some dilute ammonia is carefully added, sufficient to reduce the acidity while keeping the liquid still acid. With this treatment the colour will invariably appear either immediately or after a minute or two of further heating. The solution is allowed to boil for ten minutes, and is then covered and put aside to cool slowly. The colour comparison should never be made before the liquid has stood for at least three hours. The solution is then made up to either 500 c.c. or 1 litre in a measuring flask, and 100 c.c. of the liquid are then matched in a Nessler cylinder against $N/50$ potassium permanganate solution in a manner similar to that described under the colorimetric comparison of titania (p. 74).

It is essential in this method that 10 per cent. of free acid be present when the manganese is oxidized by the periodate, though opinions differ as to which acid should be added to achieve this concentration. Some workers insist that nitric acid should be used. The author's experience is that failure to obtain the colour often results when nitric acid is used but very rarely when sulphuric acid has been added. When titania is high, a slight white precipitate due to the precipitation of titanium phosphate may impair the colorimetric comparison, but this turbidity is removed by the addition of more sulphuric acid. In rocks with a high iron content, it is better to omit the addition of phosphoric acid and to correct for the iron coloration by adding an amount of standard iron solution to the comparison solution calculated to give it an equal concentration of iron.

PROCEDURE IF BROWN PRECIPITATE APPEARS.—Occasionally, if the concentration of manganese is too great, instead of permanganate being formed, a brown precipitate of hydrated manganese dioxide is thrown down. No amount of boiling, addition of sulphuric acid or further periodate will remove this. Instead, the following procedure must be followed: Bubble a very small amount of sulphur dioxide through the solution; just enough to decolorize the manganese tint (if any), to re-dissolve the precipitate, and to produce a brown colour. The liquid is then boiled until the brown colour disappears and no trace of sulphur dioxide can be detected by means of a film of potassium permanganate solution in a loop of platinum wire. If sulphur dioxide

is present, the permanganate will be decolorized. Continue the boiling for a further ten minutes to make sure that all sulphur dioxide has been driven off. Cool somewhat, dilute considerably, add a little more potassium periodate, heat to boiling, and the permanganate colour will be developed. If the brown colour reappears, it indicates that either the sulphur dioxide was incompletely expelled or the manganese concentration is still too high, and further dilution is required after repetition of the whole procedure. If the required dilution is going to give too deep a colour when the volume is made up to, say 2 litres, then there is too much manganese present for colorimetry, and the gravimetric methods of Chapter VIIA (6) must be adopted.

Baria.—The filter and contents are ignited in an open platinum crucible inclined at about 30° to the horizontal. As soon as all carbon has been removed, sufficient sodium carbonate is added to decompose the residue, the whole being thoroughly fused over a Teclu burner for ten to fifteen minutes. As soon as it is sufficiently cool, the melt is thoroughly leached in about 100 c.c. of hot water in a beaker set on a water-bath. The solution is filtered through a 9 cm. No. 40 paper, and washed with hot water containing a little A.R. sodium carbonate until there is no reaction for sulphate when the filtrate is run into a solution of barium chloride acidified with hydrochloric acid. Two more washings are given to make sure of the removal of all trace of sulphate for, if this is not done, the subsequent acid treatment of the residue would immediately form an equivalent amount of barium sulphate which would remain on the paper and so escape the determination. The filtrate and washings are rejected, and a 50 c.c. beaker containing a few drops of 60 per cent. sulphuric acid is placed below the funnel. The residue is then dissolved on the paper by means of a few c.c. of dilute hydrochloric acid and the paper washed several times. In most cases, the filtrate will not exceed 25 c.c., and the immediate appearance of the turbidity of barium sulphate will indicate the presence of appreciable barium. Precipitation is complete only after standing overnight. Although no barium sulphate may be visible immediately, some may come down overnight. The precipitate of barium

sulphate is then filtered through a double 40 7 cm. paper, washed with cold water, ignited over a small flame, and finally over the full bunsen flame for several minutes, cooled in a desiccator, and weighed.

If the rock contains much lime, a considerable amount of calcium sulphate will remain in the residue after filtration of the manganese solution. The fusion with sodium carbonate converts this to calcium carbonate, but the final precipitate of barium sulphate will in all probability be contaminated with calcium sulphate. *In all cases where lime is high or where the barium exceeds about* 0·15 *per cent., the barium sulphate should be purified by the following procedure.*

To the ignited barium sulphate in a platinum crucible are added 1-2 c.c. of concentrated sulphuric acid and the whole is cautiously heated over a small luminous flame. As soon as the barium sulphate has dissolved, the contents of the crucible are carefully poured, while still hot, into about 50 c.c. of cold water. The crucible is swilled out into the beaker which is then allowed to stand overnight before the barium sulphate is filtered on a double 7 cm. No. 40 paper, ignited, and weighed. By means of this purification the calcium sulphate is left in solution. In one instance a precipitate equivalent to 0·27 per cent. BaO gave 0·23 per cent. BaO on purification.

(8) Phosphorus

General.—The material is decomposed with a mixture of hydrofluoric and nitric acids and evaporated to dryness. Two further evaporations to dryness are required to convert completely the fluorides to nitrates. Phosphorus is first precipitated as ammonium phosphomolybdate and then reprecipitated as magnesium ammonium phosphate. Fluorine tends to prevent the complete precipitation of phosphorus, so a little boric acid is added to convert any fluorine present to fluoborates. Vanadium is precipitated together with the phosphorus, and its presence in appreciable amount is indicated by the deep orange colour it imparts to the otherwise yellow precipitate of ammonium phosphomolybdate,

but it remains in solution during the re-precipitation as the double salt of magnesium. If for any reason silica has not been completely removed, it also is precipitated, as ammonium silicomolybdate, and will be largely thrown down as free silica in the re-precipitation as magnesium ammonium phosphate, so that a high result will be obtained. Nevertheless, provided due care is exercised, the determination of phosphorus by the following method is extremely accurate, duplicate results differing by only one or two hundredths of one per cent.

PROCEDURE.—1-1·5 g. of powdered material are weighed into a small platinum dish. 5 c.c. of concentrated nitric acid and not less than 20 c.c. of re-distilled hydrofluoric acid are added, the mixture is stirred with a platinum stirring rod, and slowly evaporated to *absolute dryness* on the sand-bath, with frequent stirring to prevent caking. (Should the residue show a decided green tinge as soon as it is dry, this is probably an indication that an appreciable amount of copper is present.) The residue is broken up, the dish nearly filled with concentrated nitric acid, and evaporation again carried to *complete dryness*. The dish is once more nearly filled with nitric acid and evaporated to dryness. Towards the end of these last two evaporations it will be found that the mixture is particularly prone to spurt unless the heating is carefully regulated and the mixture is stirred from time to time.

The dish is nearly filled with water and heated on the water-bath for half an hour or longer, when everything should dissolve, with the exception of ilmenite, rutile, etc. The addition of a few drops of hydrogen peroxide is useful in helping to obtain a clear solution when the rock has a high content of titania.* The liquid is filtered through a 9 cm. No. 41 filter paper and well washed with hot water, the residue being rejected. Diluted ammonia (1 : 1) is added a little at a time until the nitric acid is nearly neutralized, as shown by the slow re-solution of the hydroxide precipitate. Approximately 0.5 g. of A.R. boric acid, or a grade free from phosphorus, is then dissolved in the solution, and finally 10 c.c. of a 50 per cent. solution of ammonium nitrate are added.

The precipitating solution of ammonium molybdate is then

* Personal communication from Prof. H. F. Harwood.

freshly prepared as follows : 2.5 g. of powdered ammonium molybdate* are dissolved in 12.5 c.c. of water to which a few drops of ammonia have been added. This solution, contained in a small beaker, is poured into 12.5 c.c. of concentrated nitric acid in a measuring cylinder. (This operation must not be performed the other way round.) The white precipitate which forms at first re-dissolves on stirring. *The solution must be perfectly clear.* If several phosphorus determinations are being run at the same time, the proportions may be increased accordingly and 25 c.c. of the reagent added to each solution.

The whole of the molybdate reagent is added to the phosphorus solution, the covered beaker is placed on the water-bath for one hour, and then allowed to stand overnight. In the morning the yellow precipitate of ammonium phosphomolybdate is filtered on a 7 or 9 cm. No. 40 paper and washed six or seven times with Woy's solution (see p. 11). The receiver is replaced by a 250 c.c. beaker and the residue on the paper is washed with a $2\frac{1}{2}$ per cent. solution of ammonia. When the whole of the yellow precipitate has dissolved, the paper is given two or three more washings. A few tenths of a gram of citric acid are added to prevent precipitation of any iron carried down with the phosphorus, and then 10 c.c. of the special magnesia mixture (see p. 11) plus 0.1 c.c. for every mg. of P_2O_5 expected, is added drop by drop with stirring from a pipette, as it is essential that the precipitate shall be crystalline. A few c.c. of strong ammonia are added and the solution is allowed to stand overnight.

The precipitate is filtered through a 7 or 9 cm. No. 40 paper and washed with $2\frac{1}{2}$ per cent. ammonia solution until free from chloride. It is then ignited and blasted to magnesium pyrophosphate, $Mg_2P_2O_7$, in the same way as the magnesia precipitate of the main portion.

(9) Carbon Dioxide.

General.—A qualitative test is given on p. 237. Hydrochloric acid which was formerly used for the release of carbon dioxide is now generally replaced with advantage

* Weighed out on a rough balance, since a greater quantity than this is undesirable.

by syrupy phosphoric acid, as suggested by G. T. Morgan.* The gas is absorbed in tubes packed with "Sofnolite," a variety of soda-lime in which an indicator is incorporated. When fresh the colour is green, but on exhaustion it turns first red and then brown. The efficiency of Sofnolite is shown by the fact that in a particular test two-thirds of the first absorption tube was exhausted and absorbed 1.5 g. of rapidly-passed carbon dioxide while the second Sofnolite tube gained only 0·4 mg.

Description of Apparatus and Discussion of Method. The apparatus used is shown in Fig. 9. It consists of a squat broad-necked generating flask fitted with a tap funnel which is preceded by a soda-lime guard tube A, the purpose of which is to free from carbon dioxide the air aspirated into the apparatus. B is a bubbler containing syrupy phosphoric acid to which has been added sufficient chromic anhydride to give the mixture a decidedly reddish-brown colour. This bubbler serves the triple purpose of indicating the rate of passage of the gases, removing from them any traces of hydrogen sulphide derived from pyrrhotite (as well as possible hydrocarbons), and trapping most of the water vapour driven over. After being used many times the phosphoric acid turns pale yellow and then greenish; this is a sign that it should be replaced. The gases are next dried from traces of water vapour in the tube C filled with granulated calcium chloride previously saturated with carbon dioxide by being placed in a tower up which the gas is passing. Then follow the soda-lime absorption tubes D and E. Each tube is about four-fifths filled with Sofnolite, the remaining fifth being occupied by granulated calcium chloride previously saturated with carbon dioxide. These tubes are filled, as shown in Fig. 9, a little glass-wool being used to hold the reagents closely packed. *It is essential to observe that tubes D and E are so joined that the calcium chloride comes on the outgoing side of the tube*, the reason being that the absorption of carbon dioxide by the soda-lime is accompanied by release of water which must be absorbed by the calcium chloride if it is not to escape from the tube. When a considerable amount of carbon dioxide is absorbed,

* *J. Chem. Soc.*, 1904, **85**, 1001.

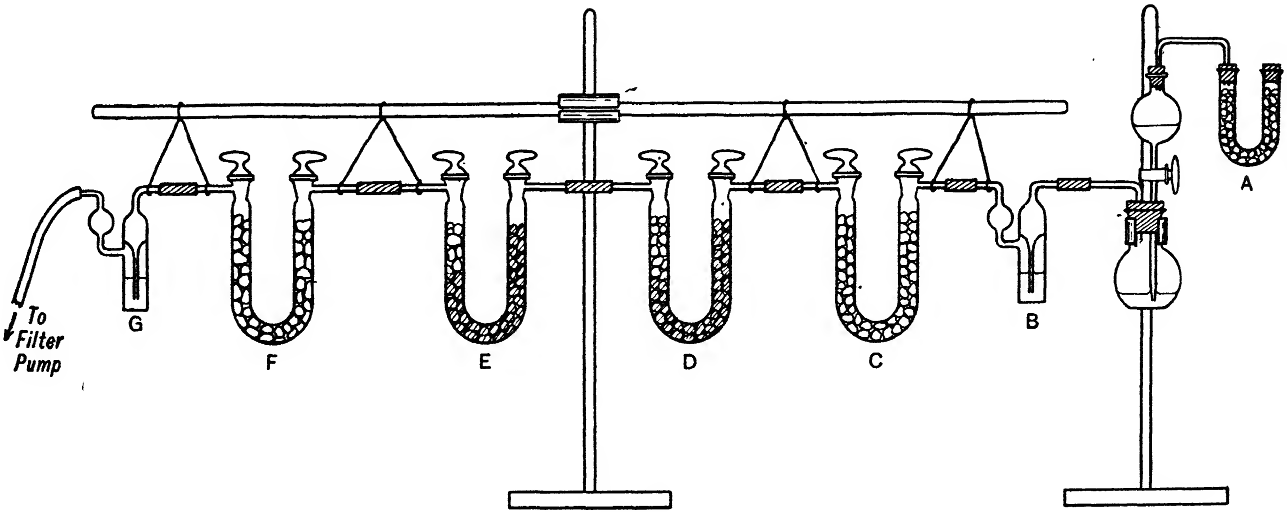


FIG. 9.—APPARATUS FOR THE DETERMINATION OF CARBON DIOXIDE.

A, Guard tube containing Sofnolite; B, bubbler containing phosphoric acid; C and F, calcium chloride tubes; E and D, absorption tubes containing Sofnolite (shaded) and calcium chloride (unshaded); G, Sulphuric acid bubbler.

the tube will become quite hot to the touch, and the calcium chloride will become noticeably moist. To guard against any carbon dioxide getting past tube D or even a little water vapour escaping from it, it is always necessary to have the second absorption tube E. Both tubes are weighed and, if the gases have not been passed too rapidly, the weight of tube E will not change by more than one or two tenths of a milligram. A greater increase of weight than this indicates either that the gases have been passed through too rapidly or that the contents of tube D are becoming exhausted and need replenishment. Tube E thus acts as an indicator of the efficiency of the apparatus. F is another calcium chloride tube, the purpose of which is to prevent water vapour from the filter pump passing back into the absorption tubes. G is another bubbler, of the same size as B but filled with sulphuric acid to prevent water vapour passing back into the tubes. This last bubbler serves a further extremely useful purpose in that it enables the worker to compare the rate of bubbling in B and G, which should be equal when all taps are open ; unequal bubbling is a sure indication of leakage. When necessary, G is attached to a filter pump. The generating flask is clamped to a retort stand, and the absorption train is conveniently suspended by copper wire from a stout glass rod clamped in a horizontal position.

This apparatus, when properly set up, can be extremely efficient, the degree of efficiency being visible all the time if Sofnolite and the bubblers are used as described ; weighing of the second absorption tube E affords the final proof of accuracy. By this method a few hundredths of one per cent. of carbon dioxide can be accurately determined provided a 2 g. sample is used. When many determinations have to be made they can be done at the rate of one an hour. The apparatus can be kept permanently set up with tubes D and E stored in the balance case. The only drawback is, perhaps, the size of the apparatus when laboratory space is very limited. In such cases the worker may be interested in the method devised by M. H. Hey.*

PROCEDURE.—**Set up the apparatus, close the tap of the**

* *Mineralog. Mag.*, 1935, **24**, 76-83.

funnel but open all the other taps. Connect the filter pump and apply a moderate degree of suction, not by any means the full force of the pump, but a suction several times greater than that to which the apparatus will be subjected in ordinary use. Test for leaks. By manipulating the taps leakages can soon be located. Render the apparatus air-tight and grease the stopcocks, but do not leave an excess of grease protruding outside. Close exit tap of tube F before turning off the filter pump. Close all taps. Detach tubes D and E, and allow them to stand half an hour in the balance case before weighing. Open one tap momentarily just before weighing either D or E.

In the meantime detach the generating flask and weigh into it 2-3 g. of the sample if the carbon dioxide content is known to be very low ; if appreciable, the sample is reduced accordingly. The flask is replaced in position, the funnel filled with phosphoric acid, and the guard tube A fixed in place. The weighed absorption tubes D and E are put into position, care being taken to see that they are the correct way round (see p. 110). The filter pump is kept in readiness but is not attached to the apparatus at this stage.

The taps of all four absorption tubes are opened and the funnel is turned on allowing the phosphoric acid to run in on the sample. Observe the rates of bubbling in B and G ; they should be equal at this stage before any carbon dioxide is evolved. As soon as all the phosphoric acid has flowed in, the tap of the funnel is closed. If a high proportion of carbonate is present, there may be a sufficiently rapid generation of gas at first without the application of heat ; otherwise the bare flask is gently warmed by passing a small bunsen flame to and fro underneath. By a judicious application of heat to the flask, the rate of bubbling is not allowed to exceed two bubbles per second. The heating is continued thus until at the end of ten minutes, or longer if much carbonate is present, the liquid in the flask comes to the boil and is maintained in that condition for three minutes to expel the last traces of gas from the liquid.

The flame is then taken away from the flask and, as the liquid in the bubbler B begins to suck back into the upper part of the bubbler, the tap of the funnel is opened. The

cooling of the contents of the flask will draw in air for the next half minute or so, meanwhile the filter pump is attached and turned on very gradually so as to maintain the same rate of bubbling (one to two bubbles per second) while air is being drawn through the apparatus. The tap of the funnel can also be used to control the rate of bubbling. Air is drawn through in this manner for ten minutes, when the exit tap of F is closed, followed by the closing, in order, of the other seven taps of the absorption tubes. D and E are disconnected, and placed in the balance case for half an hour. At the end of this time they are wiped with a clean *linen* handkerchief and weighed, one tap being opened momentarily before weighing to restore atmospheric pressure. The sum of the increase of weight in D and E represents the carbon dioxide, less a correction for the blank. Meanwhile the flask may be washed out, dried on the air supply for the blast, and the sample weighed in readiness for the next determination. If the apparatus is not to be used again for some time, the entrance to the guard tube A should be closed.

BLANK.—A blank determination should be run under the same conditions as those of the actual experiment and the gain in weight in D (there should be no gain in E) noted and deducted from the amount of CO_2 found each time. If the apparatus is used in a crowded laboratory where there are many gas burners in operation, the blank will be a milligram or more, but in a room with a low carbon dioxide content the blank will be negligible for all but the most accurate work.

Note.—The above method fails to release the carbon dioxide contained in scapolite which requires hydrofluoric acid for its decomposition, in which case a modified absorption train is then required. For details, see Hillebrand, *Bull*, 700, *U.S. Geol. Survey*, p. 219.

(10) NON-CARBONATE CARBON

Non-carbonate carbon in rocks, including graphite, is usually determined by means of wet combustion — viz., oxidation to carbon dioxide by chromic acid and phosphoric acid, the gas being absorbed and weighed in soda-lime tubes.

General Considerations.—B. E. Dixon, who has made a study of the determination of non-carbonate carbon in rocks, shows* that it is difficult to attain complete combustion to carbon dioxide by wet combustion with chromic and sulphuric or chromic and phosphoric acids. The losses are due to formation of carbon monoxide and possibly of acetic acid, and to distillation of volatile hydrocarbon. He obtained satisfactory results by interposing a second reaction flask of chromic and phosphoric acids plus a mercury catalyst between the decomposition flask and the absorption train. Dixon's figures show that the results obtained when using one flask only may be several per cent. low. For rocks or minerals with a high percentage of non-carbonate carbon such as graphite, highly graphitic schists, bitumen and bituminous rocks, sands and shales impregnated with oil, lignite, and coals, the method described by Dixon, using two flasks, should be followed ; for the much more common case where the carbon content is only a few per cent., or less than 1 per cent., results of sufficient accuracy will be obtained with the apparatus described below, using only one flask. Whichever method is adopted carbon dioxide can be determined first, followed by the addition of chromic acid and the carbon determination.

Description of Apparatus.—The apparatus is the same as that used for the determination of carbon dioxide as shown in Fig. 9 except that the flask is replaced by one of different type, and that a plain 6-inch **U**-tube is interposed between the flask and the bubbler containing phosphoric acid and chromic acids (see Fig. 10).

The special generating flask is a round-bottomed one of 300 c.c. capacity fitted with a 50 c.c. tap funnel ground into the neck and a side-arm acting as delivery tube to the plain **U**-tube. This arrangement, introduced by Prof. H. F. Harwood, avoids the use of rubber bungs or tubing in the vicinity where spray from the chromic acid mixture is likely to come into contact and cause a high or somewhat variable blank. It is as well to have the delivery tube as high up in the neck of the flask as possible to reduce the amount of water carried over. The large **U**-tube serves to

* *Analyst,* 1934, **59,** 739-743.

condense the fairly considerable amount of water which distils over. The tap funnel is preceded by a soda-lime (Sofnolite) guard tube.

PROCEDURE.—If only 0·1 per cent. or so of carbon is expected, 2 g. or more of the powdered sample from a specimen tube are weighed by difference into the flask. If the carbon content amounts to several per cent., take only 0·5 g. The tap funnel is filled with syrupy phosphoric acid (sp. gr. 1·75) and the carbon dioxide determination carried out as described on pp. 112-114. When the carbon dioxide has been weighed

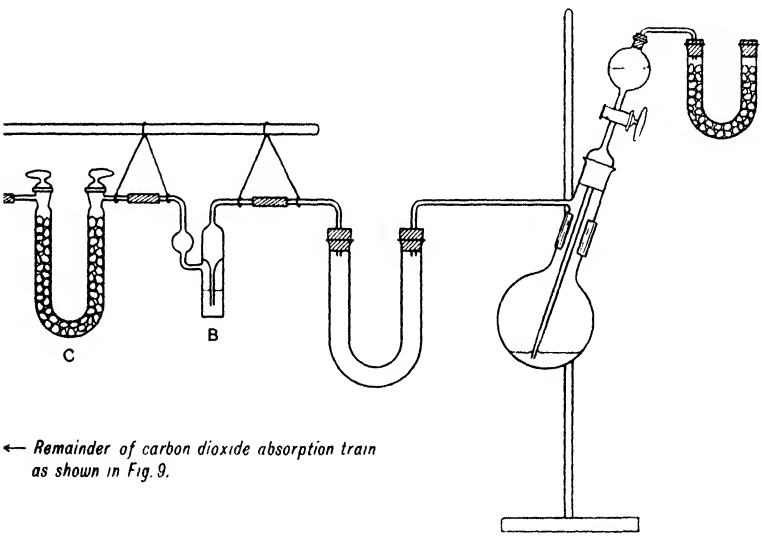


FIG. 10.—APPARATUS FOR DETERMINATION OF NON-CARBONATE CARBON.

and the absorption tubes replaced in position, the tap funnel is momentarily withdrawn from the generating flask and 3 g. of *pure* chromic acid added. If free sulphur is present in the sample, additional chromic acid should be used.

When much carbon is present, the reaction is apt to start violently. Heating is commenced, therefore, with a luminous flame not more than 1 inch in height, the top of the flame being 2 to 3 inches below the flask. The heating is arranged so that not more than two bubbles per second pass through the bubblers. The reaction tends to go very rapidly as soon

as the temperature is about 60-80° C. and great care is needed to control it at this stage. The heating is continued with a gradually increasing flame until the liquid in the flask has changed from reddish-brown to deep green, and continued for a further half an hour. The whole operation takes from two to three hours. During the last hour when little or no gas is being evolved, care must be taken to prevent the flask being unduly cooled by draughts, otherwise the bubblers may suck back. Air is then drawn through the apparatus for ten minutes and the absorption tubes weighed as for the carbon dioxide determination. The increase in weight represents the carbon dioxide formed by the oxidation of the carbon in the sample. If carbon dioxide was not expelled first, it will of course be included in this weight.

The amount of carbon present in a rock is usually much less than is at first expected: for instance, a shale containing 0·3 per cent. C will probably appear nearly as black as coal.

BLANK.—A blank determination must be run under exactly the same conditions as the actual determination, and the amount of carbon dioxide found deducted. The blank is usually in the neighbourhood of 3 mg. The use of a rubber stopper and connecting tube on the flask will raise the blank, though the other rubber connections do not seem to matter, probably due to the fact that spattering from the acid cannot reach them.

(11) SULPHUR

Sulphur may be present in rocks and minerals in the native state, as a sulphide which is usually soluble in aqua regia, or as a sulphate. Of the latter, barytes ($BaSO_4$) and celestite ($SrSO_4$) are insoluble in acids and stable up to a red heat; gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), haüyne ($Na_2Ca(NaSO_4.Al)Al_2(SiO_4)_3$), and nosean are soluble in acids;* epsomite, glauberite, and a number of normal hydrous sulphates are soluble in water; certain basic hydrous sulphates such as alunite $K_2Al_6(OH)_{12}(SO_4)_4$ are

* Some scapolites contain appreciable SO_3 but most of them are decomposed only incompletely by hydrochloric acid.

soluble only in sulphuric acid but give off water and sulphur trioxide on ignition. Neglecting for the moment the special cases dealt with in Chapter VIII (*g*), it follows that the determination of sulphur may be :

(*a*) For the total sulphur, including barytes or celestite, and the insoluble basic sulphates — *e.g.*, alunite, and natroalunite.
(*b*) For the acid-soluble sulphur mainly in sulphides.
(*c*) For the sulphur trioxide in acid-soluble sulphates.

Thus, if the sulphur in a rock is present both in sulphide form as pyrite and as the insoluble barytes, by carrying out determinations (*a*) and (*b*) and taking the difference, the amount of both types of sulphur is found. This determination of both types of sulphur should be undertaken when the rock is known to contain both a sulphide mineral and an appreciable amount of barium. It is then possible to calculate how much of the barium is present as barytes and how much as silicate or possibly carbonate. Such data on the mineralogical location of barium are of considerable interest to the petrologist. *For cases where free sulphur is present, turn to Chapter VIII (g).*

(a) *Total Sulphur*

A sodium carbonate fusion and subsequent leaching in water brings into solution in sulphate form all sulphur present in a rock and allows of precipitation as barium sulphate. The method to be described is highly accurate provided adequate precautions are taken to prevent the entry of extraneous sulphur.

PROCEDURE.—**A 1 g. sample is fused with 8 g. of A.R. sodium carbonate in a closed platinum crucible over an alcohol bunsen burning rectified spirit—not methylated spirit, which contains sulphur. Potassium carbonate and fusion mixture, although more readily fused over an alcohol bunsen, unless fresh and sulphur-free, are not to be recommended, as they are prone to take up sulphur from gas fumes while in stock. The fusion is always carried out for the same length of time, say forty minutes, as a blank has to be done**

afterwards. Nowadays most laboratories are equipped with an electrically heated crucible or muffle furnace, which, if properly handled, can be used in place of an alcohol bunsen.

The cooled melt is completely leached with hot water in a platinum dish on an electrically heated water-bath or at the steam jet. The liquid is filtered through a No. 40 filter paper and the residue well washed with hot water.* The volume of the solution plus washings should be about 200-250 c.c.; if much smaller, silica is prone to separate on subsequent acidification. A little methyl red is added and the liquid acidified with hydrochloric acid (tested sulphur free). The beaker is covered with a clock glass, and the contents brought to the boil as speedily as possible over an ordinary gas burner. A moderate excess of warm barium chloride solution is added, and the whole is allowed to stand for several hours before filtering through a double 40 filter paper, washing with cold water, ignition, and weighing as $BaSO_4$.

If there is any suspicion of contamination with silica, a drop of dilute sulphuric acid (1 : 1) and several drops of hydrofluoric acid are added, evaporated over a small flame, the residue re-ignited and weighed.

BLANK.—A blank determination is carried out using the same weight of sodium carbonate, fused for the same length of time, using the same volume of liquid, the same amount of acid, and heating for the same time over the gas bunsen to bring to the boil, etc. The blank so found will remain fairly constant provided that the same reagents are used under similar conditions every time. The blank is mostly dependent on the sulphur content of the flux.

(b) *Acid-Soluble Sulphur*

2 g. of rock powder (less if much sulphide is visible) are weighed into a 100 c.c. beaker and 20 c.c. of aqua regia added (15 c.c. of concentrated nitric acid and 5 c.c. of concentrated hydrochloric acid — both previously tested for freedom from sulphur). The beaker is covered with a watch glass and gently heated over a steam jet or electrically

* Zirconia, baria, and rare-earths may be determined in this residue (see p. 121).

(not gas) heated water-bath until the vigorous reaction with evolution of nitrous fumes is over. By careful manipulation of the valve on a steam jet this reaction should not get out of control even when much sulphide is present. The watch glass is then removed and the acid evaporated. 10 c.c. of concentrated hydrochloric acid are added and the cover replaced for a while until effervescence ceases. The cover is removed, rinsed into the beaker, and the excess of acid evaporated. When dry, the residue is treated with 2 c.c. of concentrated hydrochloric acid, 50 c.c. of water are added, the mixture stirred, and the liquid is digested for a further thirty minutes on the steam or electrically heated water-bath before being filtered through a No. 40 paper. The solution is then smartly heated to boiling over a gas bunsen, or better an electric heater, and a hot solution containing 0·5 g. of barium chloride in 10 c.c. of water is added, the contents of the beaker being allowed to stand overnight before filtration through a double No. 40 7 cm. paper. The precipitate is washed with *cold* water, ignited at a red heat over a bunsen, and weighed.

BLANK. A blank determination must be carried out under exactly similar conditions and the weight of barium sulphate found deducted from that in the actual sulphur determination. Several sulphur determinations by this method can be conveniently run at the same time as one control or blank.

Note.—In the case of rocks having a high content of acid-soluble iron (such as magnetite, pyrite, etc.), the large amount of ferric chloride produced by digestion with acid contaminates the barium sulphate, thus rendering the determination inaccurate. In such instances the fusion method for total sulphur (method *a*) is to be preferred.

(c) *Sulphur Trioxide in Acid-Soluble Sulphates*

The presence of acid-soluble sulphate will have been disclosed by the simple test in Chapter X.

PROCEDURE.—**1-2 g. of the powdered sample are weighed into a 250 c.c. beaker covered with a clock glass and boiled with 50 c.c. of dilute hydrochloric acid (1 : 5) for fifteen**

minutes. The liquid is filtered through a double 40 9 cm. paper, the residue and the paper being well washed. The volume of liquid should not be less than 200 c.c. in order to prevent possible precipitation of silica. The liquid is brought to boiling point in a covered beaker, the sulphur precipitated with a moderate excess of barium chloride (0·5 g. of BaCl in 10 c.c. of hot water), and allowed to stand overnight, after which it is filtered through a double 40 7 cm. paper, washed with cold water, ignited at a moderate red heat, and weighed.

If there is any suspicion of contamination with silica, a drop of dilute sulphuric acid (1 : 1) and several drops of hydrofluoric acid are added, evaporated over a small flame, and the residue re-ignited and weighed.

Note.—If the test referred to in Chapter X reveals the presence of a sulphide mineral, such as pyrrhotite (Fe_7S_8), which is decomposed by hydrochloric acid with evolution of sulphuretted hydrogen, carbon dioxide must be passed in under the cover-glass while the sample is being boiled with acid. According to Washington*, seven-eighths of the sulphur of pyrrhotite then goes off as hydrogen sulphide, the remaining one-eighth being precipitated as sulphur. If this is small in amount, it need not be filtered, as it is burned in the subsequent ignition.

(12) Total Sulphur, Zirconia, Baria, and Rare-Earths on One Sample

A method for the determination of all these constituents on one sample was devised independently by both W. F. Hillebrand and H. S. Washington. As pointed out by Washington (*op. cit.*, p. 255), the whole process, although apparently complicated, in reality adds very little extra time to an analysis, for the various operations may be carried out during pauses between the main determinations. Although a one-gram sample suffices, two grams increase the accuracy of the last three constituents.

Total Sulphur.—This is determined as described in Section 11 (a) except that the residue after fusion, leaching, filtration, and washing is preserved for baria, zirconia, and rare-earths.

* "The Chemical Analysis of Rocks," 1930, p. 262.

Zirconia.—The residue on the filter paper, referred to above, is carefully washed back into the platinum dish by means of the wash-bottle. To the contents of the covered dish, which will amount to about 50 c.c., is added just sufficient 50 per cent. sulphuric acid to dissolve the carbonates and silicates on gentle warming over the water-bath. After standing half an hour, the small insoluble residue is filtered on a double 40 9 cm. paper, washed, and reserved for the determination of baria.

The zirconia is present in the filtrate as sulphate, and is precipitated as phosphate while the titania is oxidized and kept in solution by hydrogen peroxide.

Concentrated sulphuric acid is carefully added to the filtrate in a measured amount calculated to be 9 per cent. of the filtrate by volume. 5 c.c. of hydrogen peroxide (20 volumes strength) are then added which, of course, colour the liquid yellow. About 1 g. of ammonium phosphate is dissolved in 10 c.c. of water, added to the yellow liquid, and allowed to stand overnight. If no precipitate forms, the liquid is left a further twenty-four hours before returning zirconia as absent. The gelatinous precipitate of zirconium phosphate is filtered through a 7 or 9 cm. No. 41 filter paper and washed with a cold 5 per cent. solution of ammonium nitrate to prevent the hydrolysis which takes place if water only is used. The filtrate is reserved for rare-earths. If the precipitate is appreciable, it is advisable to purify it before strong ignition in platinum to the pyrophosphate ZrP_2O_7. For purification, the paper and precipitate are ignited, the residue fused with potassium pyrosulphate, and zirconium in the solution obtained by leaching the melt is precipitated in the same way as before. It must not be forgotten that the ZrO_2 found is to be deducted from the amount of alumina.

Baria.—The residue reserved for baria contains also calcium and traces of strontia, all as insoluble sulphates. The baria is separated from this mixture in exactly the same way as that treatment of the insoluble residue from the manganese determination described on p. 106.

Rare-Earths.—A strong solution of caustic soda or potash is added to the filtrate from the zirconium phosphate

in sufficient excess to precipitate the rare-earths together with iron and titania while holding the alumina and silica in solution. The precipitate is filtered through a No. 41 paper and washed five times with hot water, after which it is transferred by means of the wash-bottle to a small platinum dish. Just sufficient hydrofluoric acid is added (but no sulphuric acid) to dissolve the precipitate, and the liquid is evaporated to dryness on a sand-bath in the fume cupboard. The fluorides of iron and titania are dissolved in a little water containing a few drops of hydrofluoric acid, and the insoluble fluorides of rare-earths are filtered on a No. 40 7 cm. paper supported in a rubber funnel, the filtrate being caught in a platinum dish. The filter is washed, ignited in a platinum crucible, sufficient 50 per cent. sulphuric acid is added to decompose the fluorides and the whole evaporated to dryness over a small flame. The small residue is dissolved in a very little dilute hydrochloric acid, transferred to a 100 c.c. beaker, and the rare-earths precipitated as hydroxides with a slight excess of ammonia. The hydroxides are filtered on a 7 cm. 41 paper, washed twice with water, dissolved on the filter in a little dilute hydrochloric acid, the solution evaporated to dryness, and the residue heated with a few drops of oxalic acid solution. The rare-earths remain as insoluble oxalates, anything else present being soluble. The rare-earth oxalates are filtered on a 7 cm. No. 40 paper, ignited, and weighed as $(Ce,Y)_2O_3$. Actually the residue consists of m CeO_2 and n Y_2O_3, but the reduction of CeO_2 to Ce_2O_3 is needless for the small quantities found in rocks. It is advisable to confirm the rare-earths by dissolving the residue in hydrochloric acid, precipitating by ammonia, solution and re-precipitation as oxalate.

(13) Fluorine. Gravimetric Method

General.—The following method is unsuitable only when small amounts of fluorine (less than 10 mg.) are present. In these cases the colorimetric method described in Chapter VII is generally considered to be the more accurate, and with this the author's observations are in agreement.

The gravimetric method here presented is that of Berzelius

described by Hillebrand,* with an improvement introduced by J. I. Hoffman and G. E. F. Lundell† in that zinc nitrate is used in place of ammonium carbonate to precipitate silica and alumina. The method consists of decomposition with fusion mixture followed by leaching, precipitation of the bulk of the silica still held in solution by means of zinc nitrate, and removal of the last of the silica and some phosphorus by treatment with ammoniacal zinc carbonate. Phosphate and chromate are precipitated by silver nitrate and the excess of this reagent is removed by sodium chloride. A little sodium carbonate and an excess of calcium chloride are used to bring about the co-precipitation of calcium carbonate and calcium fluoride. The carbonate is removed in weak acid which inevitably tends to dissolve a very little of the fluoride so that the method is inclined to give slightly low results. Further, there is a tendency to loss of fluorine on ignition of calcium fluoride in paper. Nevertheless, the necessity for determining fluorine is more frequent, and the accuracy of the gravimetric method is higher, than Washington indicates.‡

PROCEDURE.—**2 g. of the powdered sample are fused in platinum with specially pure fusion mixture over a bunsen or Teclu burner. The blast should not be used as some alkali fluoride may be expelled thereby.**

Hillebrand points out that "for minerals rich in fluorine and low in silica it may be necessary to add pure silica before fusing in order to effect complete decomposition of the fluoride." For rock analysis, however, it is extremely unlikely that this addition will ever be necessary.

The melt is thoroughly leached with hot water in a platinum dish stood on the water-bath, after which the solution is filtered. The residue is washed back into the dish by means of the wash-bottle, about ½ g. of sodium carbonate added, the liquid boiled for several minutes on a sand-bath, filtered, and then washed three times with hot water containing a little sodium carbonate. The filtrate is added to the previous one in a large platinum dish, 20 c.c. of the special zinc nitrate

* Hillebrand-Lundell, 1929, p. 800.

† *Bur. of Standards Journ. of Res.*, 1929, 3, 581; Hillebrand-Lundell, 1929, 805.

‡ "The Chemical Analysis of Igneous Rocks," 1930, p. 264.

solution (see p. 12) are added, the whole boiled on a sand-bath for several minutes, filtered through a 12·5 cm. No. 41 paper into a conical flask, and the bulky precipitate washed three times with hot water. The flask and its contents are cooled under the tap and transferred to a large platinum dish. A few drops of methyl orange are added as indicator, and the solution is carefully neutralized with *nitric acid* for phosphorus has still to be removed. A solution of sodium carbonate is added until the liquid is just alkaline, when a further 0.1 g. of the solid reagent is added and dissolved.* 1 g. of pure zinc oxide and a lump of pure ammonium carbonate are placed in a test-tube, which is then two-thirds filled with water, a few c.c. of 1 : 1 ammonia added and the whole warmed by immersion in the water-bath until, after a few minutes, complete solution results. If solution of the oxide is difficult, add a little more ammonium carbonate. The whole of this solution is added to the contents of the dish which are then covered with a clock glass and boiled on a sand-bath until such time as the ammonia is *completely* expelled. Water is added from time to time to replace that lost by evaporation for the process takes about two hours. This precipitates the last of the silica and some phosphorus. The precipitate is filtered through a No. 41 paper and washed three or four times with hot water.

Phosphorus and chromium are next removed by the addition of a moderate excess of silver nitrate solution, warming on the water-bath and stirring until the precipitate has quite coagulated, and filtering through a No. 40 9 cm. paper. If it has already been proved that only a negligible amount of phosphorus and chromium is present (not exceeding 0·05 per cent. of P_2O_5 and Cr_2O_3), this step can be dispensed with, but this state of affairs will rarely be encountered even in the analysis of a purified sample of amphibole or pyroxene. The excess of silver is precipitated with a solution of A.R. sodium chloride, and after half an hour or so of heating and

* This modification is adopted by Prof. Harwood in place of that given by Hillebrand-Lundell (p. 801) and Washington (p. 265), who use phenolphthalein as indicator and boil after neutralizing with nitric acid and adding a few further drops of nitric acid to discharge the red colour should it reappear. The latter authors, it will be recalled, use ammonium carbonate instead of zinc nitrate.

stirring to coagulate the precipitate, the silver chloride is filtered on a No. 40 11 cm. paper, and washed three times with hot water containing a little A.R. sodium chloride.

The filtrate, which contains alkali carbonate and fluoride but no ammonium salts, is evaporated in a platinum dish to a volume of about 150 c.c., 5-10 mg. of sodium carbonate are added, followed by 20 c.c. of a 10 per cent. solution of calcium chloride, $CaCl_2.6H_2O$, after which the liquid is boiled. The addition of the sodium carbonate is for the purpose of co-precipitation of calcium carbonate which helps with precipitation of the calcium fluoride. There must be no ammonium salts in the solution at this stage or calcium fluoride will tend to be held up. An excess of calcium chloride must be present, but a larger amount than that just mentioned will rarely be required except in the analysis of some fluorine-rich micas, topaz, etc., for 30 c.c. of a 10 per cent. solution is sufficient for 0·1 g. of fluorine. If there is no precipitation within a few minutes, a little more dilute sodium carbonate is added until a slight, finely divided precipitate appears, but an excess of the solution should be avoided. Neither Hillebrand nor Washington mentions the time to be allowed for precipitation but it is clearly advisable in accurate work to let the liquid stand overnight as recommended by Harwood.*

The precipitate is filtered through a small No. 40 paper, washed several times with water, and then ignited at as low a temperature as possible in a 2-3 inch platinum dish. 5-10 c.c. of water are added according to the bulk of the precipitate, and 30 per cent. acetic acid is added drop by drop until the calcium carbonate is all dissolved as shown by the absence of effervescence on the addition of a further two or three drops. A greater excess of acetic acid than this should be avoided. The liquid is evaporated to dryness on the water-bath to insure the complete solution of the calcium carbonate and to convert the calcium fluoride to the granular form, and the residue leached in a little water containing one drop of acetic acid. The solution is filtered through a No. 40 7 cm. paper, and washed with water six times. The residue is ignited in

* "Practical Rock Analysis for Geologists." Publication of Imperial College of Science and Technology, 1933, p. 25.

a platinum crucible, the temperature not being allowed to exceed a dull red heat, and weighed as calcium fluoride.

If the various separations have not been perfect, the calcium fluoride will be contaminated — and in practice it frequently is — with some phosphate, silica, or calcium silicate. It is always advisable, therefore, to convert the fluoride to sulphate and ascertain the increase in weight as a check on the purity of the product. Accordingly the precipitate is covered with a few drops of concentrated sulphuric acid and the crucible, covered by a clean watch glass, is carefully heated over a small flame for five minutes. The watch glass is then washed, wiped, and examined for signs of etching, which will be observed with only a milligram or two of calcium fluoride. The excess of sulphuric acid is then removed by evaporation over a small luminous flame in the fume cupboard, with subsequent ignition to dull redness, and weighing. The weight of fluorine is then given by the formula $CaSO_4 - CaF_2 : 2F :: b - a : x$, where b is the weight of the sulphate and a that of the impure fluoride. According to Hillebrand, it is an exceptional case when there is exact agreement between the weight of fluoride and sulphate, and although with the small amounts usually met in rocks the percentage error may often be an appreciable one, it is of no great significance otherwise.

Note.—If the material contains more than 2 per cent of fluorine the requisite residues from the above method should be kept for the determination of silica as described in Chapter VIIA, Section 5.

(14) Chromium and Vanadium

If chromium alone has to be determined, this can be done quite rapidly by the first of the methods given but, when both chromium and vanadium are required, the procedure is decidedly lengthy, taking three days in all even when evaporations are carried on overnight. Unfortunately, in the analysis of natural silicates, vanadium is, if anything rather more important than chromium so that in practice the two constituents are commonly determined together by the longer method. The presence of a really appreciable

amount of chromium is indicated by the yellow colour it imparts to the filtrate after leaching the sodium carbonate melt for sulphur or fluorine. Obviously this test is rendered much more sensitive by evaporating to a small bulk.

METHOD FOR CHROMIUM WHEN VANADIUM IS NOT TO BE DETERMINED.—2-3 g.* of the powdered material are thoroughly fused with four times this weight of sodium carbonate (to which a small crystal of potassium nitrate has been added) in a platinum crucible. As soon as the melt is perfectly tranquil, the uncovered crucible is heated on the blast for ten minutes to insure complete oxidation of the chromium.

The melt is then leached on the water-bath, filtered through a No. 41 paper, and washed three times with hot water to which a little sodium carbonate has been added. Any greenish tinge in the filtrate due to sodium manganate is destroyed by the addition of a little alcohol. The filtrate is then evaporated to such a bulk that the density of the chromium yellow is suitable for colorimetric comparison with standard potassium chromate (p. 15). In the great majority of rocks the volume will have to be reduced to 25 c.c.

DETERMINATION OF CHROMIUM FOLLOWED BY VANADIUM. The following is Hillebrand's method with some modifications introduced by Prof. H. F. Harwood (*op. cit.*, p. 26). Thus Harwood replaces the fusion with 20 g. of sodium carbonate and 3 g. of sodium nitrate by one carried out in a nickel crucible with potassium hydroxide, sodium nitrite, and a little sodium carbonate. Hillebrand utters a warning against adding an excess of nitric acid on acidification of the leachings from the melt on account of the reducing action of the nitrous acid, but Harwood re-oxidizes the solution by means of a little hydrogen peroxide. Sulphur dioxide is preferred by Harwood to hydrogen sulphide for reduction of the vanadium solution.

In outline, the method consists of decomposition by fusion, leaching, and filtration, acidification with nitric acid, and removal of silica. Since the silica is liable to retain a little chromium, it is necessary to recover its chromium content

* Less if the material is expected to contain more than 0·1-0·2 per cent. Cr_2O_3.

and add this to the main solution which is then oxidized by hydrogen peroxide before the precipitation of mercurous vanadate, chromate, phosphate, molybdate, arsenate, etc. After filtration, mercury is removed by ignition and the resulting oxides are converted to their sodium salts by fusion with sodium carbonate. After leaching and filtration to remove any traces of ferric oxide, the chromium is determined colorimetrically. The solution is then acidified, reduced with sulphur dioxide, and titrated with permanganate.

In the presence of much chromium, a correction is needed for the vanadium figure as shown by Hillebrand (Hillebrand-Lundell, p. 767), but the correction is simply obtained by doing a test titration with permanganate on a like bulk of chromic sulphate at the same temperature and containing approximately the same amount of chromium.

PROCEDURE.—**30-35 g. of pure potassium hydroxide pellets are fused in a nickel crucible until the melt is quite tranquil, after which it is allowed to cool until it solidifies. 4 g. of sodium nitrite, 1 g. of sodium carbonate, and 5 g. of powdered sample* are weighed out on top of the solidified melt, and the crucible supported in a sheet of "Uralite" so that rather less than half projects below. This arrangement is necessary on account of the marked tendency of the melt to creep over the edge of the crucible during fusion. The closed crucible is carefully heated over a rather small flame, so that the contents are kept in a fused state for one hour. The heating has to be moderate or the melt will boil over, though towards the end of the hour a somewhat higher temperature can be safely employed. In spite of the attack, an ordinary nickel crucible will usually stand up to half a dozen such fusions before failure.**

As soon as the flame is extinguished, the lid is removed in case it should stick on solidification of the contents. The melt must be allowed to cool thoroughly before being leached with hot water in a 9-inch porcelain dish. During the leaching it will be found that the ferric hydroxide, etc., tends to form a protective coating to the melt. Solution is therefore

* These quantities are for rocks with a very small content of the constituents to be sought. If it is known that they are present in greater quantity than usual, the amounts of sample and reagents can be reduced accordingly.

accelerated by constant removal of this coating by means of a glass rod. The liquid is filtered through a 15 cm. No. 54 Whatman paper (a grade which withstands the action of solutions of caustic alkali), and the residue washed five times with a hot solution of dilute sodium carbonate. The filtrate is then acidified with an excess of nitric acid and evaporated overnight in a large porcelain dish on the water-bath. This evaporation, however, is insufficient to dehydrate the silica satisfactorily and it is always necessary to bake the residue on the sand-bath in order to drive off the last of the nitric acid. On baking, the mass becomes pasty and should be continually stirred and broken up with a stout glass rod, when it will gradually become granular and powdery as the nitric acid is removed. When absolutely dry, the residue is treated for the removal of silica (see p. 53) but using nitric acid in place of hydrochloric.

To recover the chromium which it may retain, the silica is volatilized in the usual way with hydrofluoric acid and a few drops of sulphuric. After the evaporation and ignition, the residue is fused with just sufficient sodium carbonate to decompose it, leached with water, filtered, and the filtrate added to the main one from the silica.

The solution is then transferred to a 6-inch platinum dish and carefully neutralized with a strong, freshly prepared solution of sodium hydroxide, a very slight excess being added. If any chromium is present the change to alkalinity is shown by the colour of the solution turning from pale yellow to deep yellow, corresponding to the change to chromate. 5-10 c.c. of hydrogen peroxide are added to oxidize the salts, and the liquid boiled on a sand-bath until the surplus hydrogen peroxide is all decomposed. A slight precipitate of the hydroxides of manganese and aluminium may appear but is disregarded. The solution is tested to make sure that it is still alkaline after the boiling. If not, a few drops of sodium hydroxide solution are added, but it is unwise to make the liquid too alkaline or the resulting precipitate on the addition of mercurous nitrate will be very bulky and difficult to filter. A solution of mercurous nitrate is prepared by dissolving 5-7 g. of the salt in a test-tube with one or two drops of concentrated nitric acid and 10 c.c. of

water, warming until dissolved, and then adding about half a test-tube full of water. If the solution is too alkaline and results in an unduly bulky precipitate, adjust the alkalinity by cautious addition of dilute nitric acid. The dish is heated on the water-bath until the precipitate coagulates, when it is put aside overnight.

The precipitate of mercurous vanadate, chromate, phosphate, etc., is filtered in an ordinary funnel fitted into a filter flask attached to a filter pump. The filter paper, if an ordinary one, should be reinforced with a special toughened tip or a No. 54 paper may be used without a tip. As little suction should be used as is actually required to maintain a reasonable speed of filtration. The precipitate is well washed with a cold 2 per cent. solution of mercurous nitrate.

Mercurous nitrate wash liquid tends to get too acid and may dissolve some of the precipitate, causing a turbid filtrate. The wash liquid cannot be made neutral but very dilute ammonia may be added until the basic salts just commence to appear. The solution may be slightly turbid but on standing the turbidity will probably disappear. The precipitate is then dried before careful ignition in a platinum crucible to expel all the mercury. As this process has a slightly deleterious effect on platinum a particular crucible should be earmarked for this process. The various mercurous salts are thus converted to the oxides of the acid radicles but these are then converted into sodium salts by fusion in the inclined, but uncovered, crucible with just sufficient sodium carbonate. With high Cr_2O_3 (say 0·2 per cent.), fusion for one hour is necessary in order to insure complete oxidation of the chromium to chromate. With small amounts, half an hour is probably sufficient. The melt is leached in as little hot water as possible (especially if very little chromium is present). The solution is filtered through a 7 cm. No. 40 paper to remove traces of ferric oxide, and the residue washed with 2 per cent. sodium carbonate solution. *A No.* 41 *paper is apt to pass iron which renders colorimetric comparison inaccurate and on acidification gives a high value for vanadium.* If there is not the slightest tinge of yellow in the solution, chromium is absent. For the amount of chromium usually present in rocks the solution need be

made up to only 25 c.c. and the colorimetric comparison made with standard potassium chromate solution. For larger amounts of chromium there should be greater dilution and an aliquot part taken.

The determination of chromium in this manner on a 5 g. sample is extremely accurate. While the accuracy may not always be quite to one-thousandth part of 1 per cent., nevertheless the author maintains that the third figure should be given as it can be of considerable assistance to the petrologist for whom the figures 0·007 and 0·034 per cent. Cr_2O_3 may hold more meaning than 0·01 and 0·03 per cent. respectively.

Tests for molybdenum and arsenic may be conveniently carried out at this stage. For this the solution is acidified with sulphuric acid, saturated with hydrogen sulphide in a pressure bottle, filtered, and particularly well washed (with water freshly saturated with hydrogen sulphide) in order to remove phosphate and traces of alumina. The paper is torn into two parts, one portion tested with nitric acid for the blue molybdenum coloration as described on p. 245, and the other tested for arsenic as follows: After treatment with fuming nitric acid, drive off most of the acid, dilute, filter, add an excess of ammonia and magnesia mixture. A white crystalline precipitate on standing is due to arsenic, provided all phosphorus was washed out of the sulphide precipitate. If appreciable arsenic is present, it will give a yellow tint to the sulphide precipitate.

If the tests for molybdenum and arsenic are not carried out, the solution is acidified with sulphuric acid, transferred to a small Pyrex flask with wash-bottle tubes (preferably fused through a ground stopper after the manner of the flask used for the hydrogen sulphide reduction of total iron) and sulphur dioxide bubbled through for two minutes. The contents of the flask are then boiled in a current of carbon dioxide until no more sulphur dioxide is expelled as shown by the absence of any decolorizing effect on a drop of weak permanganate solution on a loop of platinum wire. Similarly, if the solution was tested for molybdenum and arsenic, the hydrogen sulphide is expelled by boiling in a stream of carbon dioxide.

In either case care must be taken to ascertain that the last trace of either sulphur dioxide or hydrogen sulphide is removed before the solution is titrated at about 80° C. with *N*/50 potassium permanganate (1 c.c. = 0·0015 g. of V_2O_3). The reduction and titration should always be repeated, for the second titration is usually a trifle lower than the first and is taken as the correct value. The high results of the first titration are caused by the extraction of oxidizable matter from the filter paper* and, if hydrogen sulphide is used as the reducing agent, by the formation of polythionic compounds during the reduction.†

If the quantity of permanganate solution used in the titration is very small indeed, it is advisable to apply a confirmatory test for vanadium. The solution is evaporated in a porcelain dish, most of the sulphuric acid fumed off and a little water added after cooling. 2-3 c.c. of concentrated nitric acid are added, followed by a little hydrogen peroxide, when a characteristic reddish-brown colour develops if vanadium is present. If the vanadium content is at all appreciable, there is no need to concentrate and remove sulphuric acid before carrying out this test. Moreover, with practice the depth of colour produced will afford some check on the accuracy of the figure obtained for vanadium.

THE DETERMINATION OF MINUTE QUANTITIES OF CHROMIUM.—The method given on p. 128 for the determination of chromium when vanadium is not to be determined clearly has a lower limit set by the need, when minute amounts of chromium are to be determined, to evaporate the solution to such a small bulk that turbidity develops through precipitation of sodium carbonate with consequent impairment of the colorimetric comparison. By keeping the amount of sodium carbonate used to a minimum, the lower limit for chromium is probably around 0·03 per cent. Cr_2O_3. Moreover, with considerable amounts of chromium, 0·5 per cent. or more of Cr_2O_3, error due to incomplete oxidation of chromium to chromate may become excessive.‡ The method, therefore, should be regarded as a rapid one of

* R. S. MacBride and J. A. Scherrer, *J. Am. Chem. Soc.*, 1917, **39**, 928.
† G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, 1921, **43**, 1560.
‡ A. J. van der Merwe. *Trans. Geol. Soc. S.A.*, 1945, **48**, 15-16.

moderate accuracy between these limits of chromium content. The succeeding method given on pp. 129-132, however, although admittedly lengthy and tedious, affords considerable accuracy when 5 g. samples are taken, and it gives both chromium and vanadium. In recent years the utilization of organic reagents has rendered available additional methods for chromium. In that given below* the diphenyl-carbazide colour reaction is utilized; but while it enables very small quantities of chromium to be determined with the greatest accuracy, it still leaves vanadium to be determined either by the method of pp. 129-132 or by the ethyl acetate separation described on p. 135. Since these last two methods allow of the determination of both chromium and vanadium, they are likely to be the most frequently used.

Another modern method (see p. 138) is that of E. B. Sandell (Colorimetric Determination of Traces of Metals, New York, 1944, pp. 196 and 440; *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 336). It is strongly recommended, for by its means either chromium or vanadium, or both elements can be determined; it is likely to replace the old procedure of pp. 129-132 for the determination of these elements in rocks.

PROCEDURE.—**0·5-1 g. of the finely powdered sample is evaporated to dryness once only with hydrofluoric acid and a few drops of sulphuric acid in a platinum dish on a sand-bath. Potassium pyrosulphate is then added to the residue and fused in the usual manner until a clear melt is obtained. The cooled melt is then dissolved in dilute hydrochloric acid, when everything should go into solution, even if chromite is known to be present.**

The solution is diluted to a suitable volume, a few drops of strong nitric acid added, the liquid boiled for a minute and ammonia (1 : 1) carefully added from a tap funnel until precipitation is complete, the pH being kept as low as possible, *i.e.*, **until litmus just turns blue. The liquid is filtered through a 41 Whatman paper and the precipitate thoroughly washed with hot 2 per cent. ammonium sulphate solution. The precipitate is dissolved in dilute sulphuric acid and the**

* C. F. J. van der Walt and A. J. van der Merwe. *Analyst*, 1938, **63**, 809-811.

ammonia precipitation and washing repeated. The filtrates are rejected and the precipitate is once more dissolved in sulphuric acid. In this way chlorides are totally removed and the solution should not now contain more than a trace of manganese.

The solution is then diluted so that the total amount of concentrated sulphuric acid present amounts to 5 per cent. of the total volume of liquid. It is heated to boiling, 5 drops of concentrated nitric acid, 1 c.c. of a 2½ per cent. solution of silver nitrate, and 20 c.c. of a freshly prepared 10 per cent. solution of ammonium or potassium persulphate are added, and the boiling continued for 10 minutes in a covered beaker. The presence of only traces of manganese at this stage is of little consequence, as the slight pink colour will be scarcely noticeable in the aliquot part subsequently taken for analysis. To the cooled liquid is added sodium carbonate powder a little at a time until a slight excess is present. The iron and aluminium so precipitated are not filtered off but instead the contents of the beaker are transferred to a 100 or 200 c.c. graduated flask, made up to the mark, and then filtered through a dry filter into a dry stoppered flask.

50 c.c. of the filtrate are transferred to a 100 c.c. stoppered graduated cylinder, 10 c.c. of 1 : 1 sulphuric acid, and 5 c.c. of freshly prepared 0·1 per cent. solution of diphenyl-carbazide are added, and the volume is made up to 70 c.c. The violet coloured solution is then compared in a colorimeter with that of a standard potassium dichromate solution (containing 0·002 mg. of chromium per c.c.) treated in the same way.

On standing, a solution of diphenyl-carbazide turns pink by partial decomposition, but this is stated not to affect the determination. In the analysis of rocks containing more than 5,000 parts per million of Cr_2O_3, the aliquots taken for comparison with the standard should contain, after addition of acid and dilution to ± 60 c.c., less than 0·000125 g. Cr_2O_3 per c.c. ; otherwise the diphenyl-carbazide is totally decomposed and no violet colouration is obtained.*

THE SEPARATION OF SMALL AMOUNTS OF CHROMIUM FROM VANADIUM WITH ETHYL ACETATE.—In the following method,

* *Trans. Geol. Soc. S.A.*, 1945, 48, 16.

due to Margaret D. Foster,* the solubility of blue perchromic acid in ethyl acetate is utilized as a means of separating chromium from vanadium. The blue perchromic acid, formed when hydrogen peroxide is added to an acid solution of a chromate, increases in stability with decrease in the acidity of the solution. When a slightly acid solution containing chromate and vanadate ions is mixed with ethyl acetate, hydrogen peroxide added, and the mixture shaken vigorously, all the perchromic acid is dissolved in the ethyl acetate without loss from reduction. Vanadium remains in the water layer and may be drawn off and determined. The perchromic acid in the ethyl acetate layer may be reconverted to chromate by the addition of a 10 per cent. potassium hydroxide solution. On vigorous shaking the chromate dissolves in the aqueous solution and may be drawn off and determined.

The advantage of this method is that no correction need be applied to the vanadium figure for the effect of the chromium present, (*cf.* p. 129) since the two metals are effectively separated before the determination of either is commenced. Because of the relatively low solubility of perchromic acid in ethyl acetate (equal to about 1 mg. of Cr_2O_3 in 15 c.c.), the method is practicable for the removal of only very small amounts of chromium.

Procedure.—For most rocks, decomposition by fusion with sodium peroxide is recommended, but, whichever method is employed, it is essential that the resulting solution be free from iron, titanium, and manganese, and be very low in acidity.

0·4 g. of the powdered sample is mixed with 2 g. of sodium peroxide in an iron crucible, the mixture covered by a further 1 g. of sodium peroxide, and fused. The cooled melt is extracted with water containing a drop of alcohol to reduce manganate, digested on the water-bath for half an hour, filtered, and washed. The filtrate is carefully neutralized with sulphuric acid (1 : 1) and two drops only added in excess. The solution is then evaporated to about 40 c.c. and cooled to room temperature. (It is desirable to keep

* *Contributions to Geochemistry,* 1942-45, *U.S. Geological Survey Bull. No.* 950, 1946, 15-18.

the volume of solution as low as is compatible with its salt content because ethyl acetate is soluble in water to the extent of 8 c.c. per 100 c.c. at 20° C.)

The slightly acid solution is transferred to a 250 c.c. separatory funnel, and between 80 and 150 c.c. of ethyl acetate added, the amount being judged from the depth of the yellow colour of the filtrate from the leached melt. 0·5 c.c. of 3 per cent. hydrogen peroxide is added and the funnel shaken vigorously for a few seconds. If the ethyl acetate layer does not become blue, it indicates that less than 0·014 mg. of chromium is present for each 10 c.c. of ethyl acetate taken. The lower (water) layer is transferred to a second funnel and a second extraction made, using about 15 c.c. of ethyl acetate. The water layer is then run into a 100 c.c. beaker. The ethyl acetate in the second funnel is added to that in the first, and the second funnel is rinsed into the first with two 10 c.c. lots of water. The ethyl acetate and rinse water are shaken together and the water drawn off into the beaker, which now contains all the vanadium. 5 c.c. of concentrated sulphuric acid are added to the contents of the beaker, the volume adjusted to 50 c.c., and the colour compared with standards having the same acid concentration.

1 c.c. of 10 per cent. caustic potash solution is added to the blue ethyl acetate solution and the separatory funnel shaken until the blue colour has changed to pure yellow. About 10 c.c. of water are added, the funnel shaken again, and, after separation of the layers, the aqueous layer is run into a 100 c.c. beaker. The caustic potash treatment is repeated, and the further aqueous layer run into the beaker. The ethyl acetate layer is finally washed with 10 c.c. lots of water until the washings are quite colourless, the washings being added to the beaker, which then contains all the chromium, and which, after making up to a definite volume, is ready for the colorimetric determination of chromium.

Molybdenum, if present, remains in the aqueous solution. If more than 1 mg. of Mo is present in 50 c.c. during the colorimetric determination of vanadium, correction should be made for the molybdenum present.

Sandell's Method for Small Amounts of Chromium and Vanadium

Procedure.—If only one of these elements is to be determined, 1 g. of sample is taken, but, if both elements are required, 2 g. of sample are taken and the resulting solution divided into aliquots. The sample is fused in platinum with five times its weight of sodium carbonate and leached with hot water, keeping the volume of water restricted. A few drops of alcohol are added and the liquid heated near the boiling point until all manganate has been reduced, when it is filtered through a small paper into a colorimetric flask (say, 50 c.c.) and washed with hot water containing a little sodium carbonate. The solution is then made up to the mark and divided into two equal parts if both chromium and vanadium are to be determined.

For *chromium*, one aliquot is carefully acidified with dilute sulphuric acid so that the acidity is approximately 0·2 N when the solution has been diluted to volume. The solution is swirled to liberate carbon dioxide, 1 or 2 c.c. of 0·25 per cent. diphenyl carbazide solution added, made up to 50 c.c., and mixed. The colour is compared against a standard solution. If the sample solution is red or red-brown, instead of red-violet, vanadium exceeds chromium in amount. In this case it is better to obtain the transmittancy after 10–15 minutes, when the vanadium colour will have been considerably reduced through fading.

For *vanadium*, something between a tenth and a half of the aliquot (according to the basicity of the rock) is pipetted into a small Erlenmeyer flask and a drop or two of methyl orange added. 4 N sulphuric acid is then added from a burette until the intermediate colour of the indicator is reached. The solution is then swirled to liberate carbon dioxide and transferred to a small separatory funnel. 8-hydroxyquinoline solution (2·5 per cent. in 1 : 8 acetic acid) is then added to 10–25 c.c. of the sample taken from the aliquot and 2–3 c.c. of reagent quality chloroform. After shaking for one minute to extract the blackish vanadium-oxine compound, the chloroform is allowed to settle and drawn off into a platinum crucible. The stem of the funnel

is rinsed out with 1 c.c. of chloroform, and the extraction with 8-hydroxyquinoline and chloroform repeated until the last portion of chloroform shows only a faint yellow colour due to the reagent alone.

The vanadium in the crucible is then converted to sodium vanadate by the addition of 0·1 g. of sodium carbonate to the combined extracts, evaporating off the chloroform at a low temperature, heating the crucible with a flame to destroy organic matter, and the sodium carbonate finally fused. The melt is dissolved in a few c.c. of water, and, if the solution is not clear, it is filtered through porous porcelain or sintered glass. The clear solution, having a volume of 5-10 c.c., is transferred to a flat-bottomed comparison tube, 1·0 c.c. of 4 N sulphuric acid, 1·0 c.c. of 1 : 2 phosphoric acid, and 0·5 c.c. M sodium tungstate solution added, and compared with standards similarly treated.

A convenient standard vanadium solution is prepared by dissolving 1·785 g. of pure V_2O_5, previously ignited at 500° C., in a slight excess of sodium hydroxide, adding a slight excess of sulphuric acid and diluting to 1 litre. This solution should contain 1·00 mg. of vanadium per c.c. The vanadium content can be readily checked by acidifying a 50 c.c. portion with sulphuric acid, reducing with sulphur dioxide, expelling the excess of sulphur dioxide (as described on pp. 132-133), and titrating with 0·05 or 0·1 N potassium permanganate. The 0·5 sodium tungstate solution is prepared by dissolving 16·5 g. of $Na_2WO_4.2H_2O$ in water and diluting to 100 c.c.

(15) Nickel

Nickel, in the small quantities in which it usually occurs in rocks and rock-forming minerals, is determined with great accuracy by the method of H. F. Harwood and L. T. Theobald,* which is capable of precipitating quantitatively 0·01 per cent. NiO in a 2 g. sample by means of dimethylglyoxime. Using *a*-furil dioxime, these authors claim that as little as 0·0025 per cent. of NiO can be detected.

They showed that there is usually some co-precipitation of nickel along with the ammonia precipitate but not with

* *Analyst*, 1933, 58, 673-682.

the silica, lime, or magnesia. They accordingly recommend the determination of nickel on a separate sample, and in the filtrate from the magnesia precipitation in order to correct the ammonia precipitate for nickel.

The method consists, in outline, of decomposition with sulphuric and hydrofluoric acids, removal of hydrofluoric acid, neutralization of the solution by sodium hydroxide, addition of citric acid to hold up iron, and precipitation of the nickel in a slightly acid solution by an alcoholic solution of dimethylglyoxime. The nickel dimethylglyoxime is then purified by dissolving in nitric acid, removal of all nitric acid, and re-precipitation in the presence of a little citric acid to hold up iron.

PROCEDURE.—**2 g. of the powdered sample are decomposed in a 3-inch platinum dish with 15 c.c. of sulphuric acid (1 : 1) and 25 c.c. of hydrofluoric acid (added in this order). The mixture is heated on the sand-bath and well stirred in the initial stages to prevent caking of the powder. When the rock appears to be completely attacked, a crystal of potassium nitrate is added to oxidize ferrous iron and destroy any traces of organic matter, and the evaporation is continued until the sulphuric acid fumes strongly, and so maintained for ten minutes. The liquid is allowed to cool before adding water and repeating the evaporation to fuming point. The contents of the dish are cooled, 100 c.c. of water are added, and the whole digested on the water-bath until all soluble matter has dissolved. The solution is filtered if necessary and the residue is washed with hot water. As a precautionary measure, Harwood and Theobald recommend that at this stage the insoluble residue be ignited in platinum, fused with a little sodium carbonate, the melt taken up with dilute acid, and the resulting solution added to the main one, but such treatment will rarely be required. If the residue when examined with a lens contains grains of a black mineral, then, in the opinion of the present author, it is probably desirable to carry out this further recovery.**

2-3 g. of citric acid are added to the solution to prevent precipitation of iron as far as possible (though some is usually precipitated in spite of this), and the solution is neutralized with a strong solution of freshly prepared sodium hydroxide,

methyl red paper being used as an external indicator. The solution is then re-acidified very carefully with a few drops of dilute sulphuric acid before 15 c.c. of a 1 per cent. alcoholic solution of dimethylglyoxime are added, followed by an addition of ammonia (1 : 3) from a tap funnel until an excess of a few drops is present. The beaker is set aside for twenty-four to forty-eight hours before being filtered through a No. 40 12·5 cm. paper and washed five or six times with cold water. (If much ferric hydroxide has been allowed to precipitate, this filtration will be very slow.) The washed precipitate is then dissolved on the filter in the minimum amount of hot (1 : 1) nitric acid, the filtrate and washings being collected in a small beaker. A few drops of 1 : 1 sulphuric acid are added and the solution evaporated as far as possible on the water-bath. *All nitric acid must be removed in this way.* The residue is taken up in water and usually requires filtering and washing through a 7 cm. No. 40 paper. The filtrate is kept as small as possible and should not exceed 50 c.c. in volume. About 0·01 g. of citric acid is added, followed by 5-7 c.c. of the dimethylglyoxime solution which should be added avoiding contact with the stirring rod or the sides of the beaker. If this precaution is omitted, small amounts of the dimethylglyoxime are apt to crystallize on the glass and lead to high results, since it is impossible to remove them from the nickel dimethylglyoxime by washing. A drop or two of methyl red is added, followed by ammonia (1 : 3) drop by drop from a tap funnel until the solution is just alkaline, and by two to three drops (not more) in excess. After standing overnight, the red nickel dimethylglyoxime is collected on a Munroe crucible or sintered-glass filter, washed free from sulphate by *cold* water, dried at 120-130° C. for an hour, and weighed.

The fact that the first precipitation does not give any visible red precipitate of nickel dimethylglyoxime unless there is 0·03-0·05 per cent. NiO present must not be allowed to dissuade the analyst from carrying out the second precipitation, when small quantities will probably become visible for the first time.

CORRECTION TO BE APPLIED TO THE ALUMINA.—The filtrate from the magnesia precipitate is evaporated to a small

bulk in a 9-inch porcelain dish and sufficient nitric acid is added to decompose the ammonium salts. This operation needs to be carried out with care, the dish being covered by a clock glass during the violent reaction. On account of the large volume of fumes given off this will have to be done in the fume cupboard. Sulphuric acid is then added and the mixture evaporated on the sand-bath to strong fuming. The solution is rendered only weakly acid and the nickel determined by a double precipitation with dimethylglyoxime as described above. The difference between the percentage amount of nickel oxide thus found and the total amount in the rock gives the correction to be applied on account of the co-precipitation of nickel with alumina.

(16) COPPER

Copper was formerly determined by precipitation as sulphide with subsequent weighing as oxide or possibly colorimetric comparison, but with the small amounts present in most rocks a very large sample such as 20-50 g. was necessary for accurate work. The author's adaptation to silicate analysis of the very sensitive colorimetric method for copper, using the organic reagent sodium diethyl-dithio-carbamate, enables a very accurate determination of from 0·001-0·25 per cent. of CuO on a 2 g. sample.* This organic reagent gives a yellow colour with copper in slightly ammoniacal solution. Fortunately the other metals which give a coloration with the reagent, including bismuth which gives a similar colour, can be removed by a preliminary ammonia precipitation. Thallous salts cause a serious turbidity so that it is necessary for minerals separated in Clerici solution to be washed very thoroughly with hot water before examination. Chromium, zinc, nickel, and manganese give a faint turbidity with the reagent and are incompletely precipitated by ammonia, but the amounts of these present in rocks are found to be insufficient to have a disturbing influence. The organic reagent is extremely sensitive to iron, with which it gives a brown coloration, so that removal of the

* A. W. Groves, *Mineralog. Mag.*, 1935, **24**, 35-41; T. Callan and J. A. R. Henderson, *Analyst*, 1929, **54**, 650.

undesirable constituents — particularly iron — by precipitation with ammonia has to be done thoroughly.

It was found by the author that there was always retention of copper by the ammonia precipitate, the average of sixteen experiments on rocks being 34 per cent. though in several it was as low as 10-15 per cent. It is therefore essential to re-precipitate with ammonia once or twice according to the accuracy required and to do a colorimetric comparison for each filtrate, but there is the compensating advantage that it is then possible to estimate readily the degree of accuracy already attained. Two precipitations are always necessary and the need for a third or fourth will be determined by the amount of copper present, the degree of retention of copper, and whether the result is required to one-thousandth or only one-hundredth of one per cent.

INDICATION OF PRESENCE OF APPRECIABLE COPPER.—When it is dry, the residue from the first evaporation of a rock powder with a mixture of hydrofluoric and nitric acids (in the determination of phosphorus) sometimes shows a greenish tinge, which appears to be decidedly more marked when the copper content is appreciable. This colour is never visible after the second and third evaporations, for it is then masked by the deep brown of ferric salts.

SAFEGUARDS AGAINST CONTAMINATION BY COPPER.—The use of brass sieves in the crushing of the sample should be avoided. Contamination on account of prolonged heating on a copper water-bath is reduced to a minimum in the following method in which only twenty minutes of such heating is required. Undoubtedly the safest arrangement when copper is to be determined is to use an enamelled cast-iron water-bath fitted with a set of porcelain rings. The reagents used, including the distilled water, should be tested for copper.

PROCEDURE.—**2 g. of the powdered sample are heated in a 3-inch platinum dish on a sand-bath with 15 c.c. of 1 : 1 sulphuric acid and 30 c.c. of hydrofluoric acid until the mixture fumes strongly. After cooling, water is added and the mixture again evaporated to strong fuming. The temperature is then raised to fume off the sulphuric acid. This is carried on to dryness and the residue baked for several**

hours at about 300° C. The residue should be broken down and stirred from time to time to assist in the expulsion of sulphuric acid, which must be complete. The dried cake is treated with 15 c.c. of fairly concentrated hydrochloric acid on the water-bath and after ten minutes it is diluted to about 50 c.c. and further heated until complete solution results. The liquid is filtered, and after the addition of a further 10-20 c.c. of concentrated hydrochloric acid, the ammonia precipitation is carried out as described on p. 58 but with the addition of several c.c. of 1 : 1 ammonia in excess. The liquid is then boiled for three to five minutes, filtered through a double No. 41 paper, and washed three times with boiling 2½ per cent. ammonium chloride solution containing a few drops of ammonia (the use of an indicator in the wash liquid is inadmissible). The precipitate is removed from the paper, dissolved in 5 c.c. of concentrated hydrochloric acid, re-precipitated, and filtered as before with a double filter paper. Each filtrate is made up to 250 or 500 c.c. (250 in the majority of cases), an aliquot part (100 c.c.) taken, and the colorimetric comparison made with 100 c.c. of slightly ammoniacal water into which is run a standard solution containing 0·00001 g. Cu per c.c. (see p. 16). This will indicate whether a third precipitation is required to achieve the desired standard of accuracy.

If more than 0·0001 g. Cu is present in 100 c.c., turbidity is developed with the reagent and further dilution is required. The presence of the merest trace of iron in the test solution gives a brown tint with the organic reagent which is readily detected on comparison with the other tube containing copper as the only metal. The addition of some gelatine solution increases the brilliancy of colour somewhat, thereby facilitating comparison. N. D. Sylvester and L. H. Lampitt* point out that, owing to the fact that the yellow colour of copper with sodium diethyl-dithio-carbamate is due to a colloidal precipitate, the colour shade is usually somewhat different in the blank from that which is obtained in the determination, and suggest the use of an organic solvent to overcome this difficulty. They claim increased accuracy if the solution is shaken with amyl alcohol in the Nessler

* *Analyst*, 1935, **60**, 380.

cylinder, the colour of the upper layer being viewed transversely. The amount of amyl alcohol used can be varied according to the amount of copper present so that the colour of the layer is adjusted to a suitable intensity for matching. When 10 c.c. of amyl alcohol are used, the addition of 0·0002 mg. Cu is readily detected when the amount of Cu present is not more than about 0·015 mg. Carbon tetrachloride may be used in place of amyl alcohol.*

CORRECTION FOR CuO IN R_2O_3 PRECIPITATE.—Unless the retention of copper is shown to be high even after the re-precipitation of the ammonia precipitate, a correction for copper in the R_2O_3 precipitate of the main portion (which has also been precipitated twice) will usually be unnecessary. If the degree of retention shows such a correction to be desirable for very accurate work, an approximation for this correction is obtained by determination of copper in the filtrate from the third precipitation.

(17) CHLORINE

Chlorine is usually present in rocks in a form soluble in acid such as water-soluble chlorides or silicates soluble in nitric acid (sodalite, haüyne, and the chlor-apatite of basic igneous rocks), when its extraction by nitric acid is a simple matter. The minerals of the scapolite group, however, which contain appreciable amounts of chlorine, are insoluble in nitric acid and it is then necessary to carry out a sodium carbonate fusion.

(a) *Acid-Soluble Chlorine*

2 g. of the powdered sample are weighed into a 100 c.c. beaker and treated with weak nitric acid (tested with silver chloride for its freedom from chlorine). The acid has to be dilute and the subsequent boiling brief to prevent any loss of chlorine. A suitable strength is one part of concentrated acid to twenty parts of water, and about 40 c.c. of this dilute acid are used. The liquid is carefully brought to the boil and so kept for not longer than two minutes. The liquid is filtered through a double 40 paper (a turbid

* *Chem. Age*, April 25, 1936, p. 382.

filtrate will result if only one paper is used), well washed with hot water, and the filtrate cooled. A slight excess of a clear 5 per cent. solution of silver nitrate slightly acidified with nitric acid is then added. The contents of the beaker are heated on the water-bath for an hour or so with frequent stirring until the precipitate of silver chloride coagulates and is suitable for filtration. During this process the beaker should be shielded as much as possible from light by having thick brown paper tied round it and, when the precipitate has coagulated, the beaker is stood in a dark cupboard for several hours or overnight; needless to say, there should be no exposure to fumes of hydrochloric acid or ammonium chloride. If the precipitate is weighable, it is filtered through a fritted glass filter-crucible capable of retaining a fine precipitate, washed with very dilute nitric acid (1 : 99) to remove silver nitrate, dried at 130-150° C., and weighed.

If there is some turbidity present on adding the silver nitrate but the amount of precipitate is scarcely weighable with accuracy, the liquid is not heated on the water-bath but a turbidimetric comparison is carried out as rapidly as possible before the particles of silver chloride coagulate and become unsuitable for matching. The solution is made up to a known volume and compared in Nessler cylinders, or even in two comparable beakers, with an acid solution of silver nitrate to which a very weak standard solution of sodium chloride is added. Such a turbidimetric comparison is sufficiently accurate for the very large number of rocks containing less than ·05 per cent. Cl.

(b) *Total Chlorine*

1-2 g. of the powdered sample are fused with chlorine-free sodium carbonate over a good bunsen or Teclu burner and leached with hot water. After cooling, the solution which should be not less than 300 c.c. in bulk is just acidified with nitric acid using methyl orange as indicator. The precipitation of silver chloride is carried out as in (*a*). If silica separates at any stage, it is filtered off together with the silver chloride. By thorough washing of the precipitate with hot dilute ammonium hydroxide, the silver chloride is dissolved and passes into the filtrate, from which it is

re-precipitated by acidifying with nitric acid and treating as in (*a*).

(18) Boron

Except when boron-bearing minerals are known to be present, boric oxide is rarely determined in rocks, though in glasses such as Jena and Pyrex its determination is essential. The method of Chapin has been found to be superior to all others and for details the reader is referred to Hillebrand-Lundell (pp. 612-617). The shorter method of Wherry, as modified by Sullivan and Tayler, is insufficiently accurate for scientific purposes as in rock or mineral analyses, and in glass analysis it is suitable only for routine control (Hillebrand-Lundell, p. 619).

A blank determination has always to be carried out for Chapin's method and, if modern resistance glass is used for the flask containing the material under test, a high blank is inevitable. It is preferable, therefore, to have a flask specially blown from soft glass.

In more recent years a quicker and simpler method of determining boron, has been based on the flame test of p. 239 by W. Stahl (*Z. anal. Chem.*, 1930, **83,** 268-288 ; 1935, **101,** 342-356) and further developed by H. C. Weber and R. D. Jacobson (*Ind. Eng. Chem. Anal. Edn.*, 1938, **10,** 273).

(19) Beryllia

Beryllia was formerly determined by the method of Parsons and Barnes,* based on the solubility of beryllium hydroxide in a hot solution of sodium bicarbonate, in which the hydroxides of aluminium, iron, and titanium are insoluble. The perfection of the separation of aluminium, iron, titanium, and zirconium from beryllium by means of 8-hydroxyquinoline now affords the improved method for the determination of beryllia† which is adopted here.

* *J. Am. Chem. Soc.*, 1906, **28,** 1589-1595.
† H. B. Knowles, *J. Research, National Bureau of Standards*, 1936, **15,** 87-96.

PROCEDURE.—A 2 g. sample is fused with sodium carbonate, silica removed in the usual way, and *one* precipitation made with ammonia, calcium and magnesium being removed by filtration and washing with a hot neutral solution of ammonium acetate (5 per cent.). The precipitate is transferred by means of the wash-bottle to a beaker where it is boiled for several minutes in an excess of sodium hydroxide solution, filtered through a No. 41 paper, and washed three times with hot water containing a little sodium hydroxide. The precipitate is transferred to a beaker, re-dissolved in the minimum amount of dilute hydrochloric acid, re-precipitated with boiling sodium hydroxide, filtered, and washed. The combined filtrates contain all the aluminium and beryllium, the hydroxides of iron, titanium, and zirconium being insoluble in excess of alkali.

Aluminium is then precpitated according to the procedure recommended by H. B. Knowles (*op. cit.*). To the acid solution containing not more than 0·1 g. of aluminium and 10 c.c. of hydrochloric acid in a volume of 200 c.c. are added 15 c.c. of a solution of ammonium acetate prepared by dissolving 30 g. of ammonium acetate in 75 c.c. of water. Eight to ten drops of a 0·04 per cent. solution of bromcresol purple are used as indicator and ammonia (1 : 1) is added until the liquid becomes a distinct purple. An acetic acid solution of 8-hydroxyquinoline is then run in from a burette, while stirring, in 15-25 per cent. excess of the amount necessary to precipitate the aluminium. The liquid is brought to the boil with occasional stirring, and boiled gently for one minute. After allowing the liquid to cool at 60° F. it is filtered and washed with cold water. The precipitate is then re-dissolved in hydrochloric acid, the 8-hydroxyquinoline precipitation repeated, and the two filtrates united. In this way any beryllium retained in the first precipitate is recovered.

Knowles (*op. cit.*) found that it is unnecessary to destroy the organic matter before precipitating the beryllium as hydroxide. The liquid is therefore brought to the boil and precipitated with ammonia (1 : 1), an excess of only two drops being allowed. The beryllium hydroxide is filtered on a small No. 41 paper but, as a precaution against incom-

plete precipitation, the filtrate, when cool, is treated with a few drops of ammonia and allowed to stand for twenty-four hours. The precaution is recommended by both H. B. Knowles (*op. cit.*) and M. Frommes.* The precipitate is ignited to beryllia (BeO) and weighed.

R. E. Stevens and M. K. Carron, who have made a special study of the determination of beryllium in ores† report that the 8-hydroxyquinoline method seems to result consistently in small losses of beryllia. While this may not be serious in the case of rock analyses, their paper should be studied before the analysis of beryllium-bearing minerals is undertaken.

The method of W. Stross and G. H. Osborn (*J. Soc. Chem. Ind.*, 1944, **63,** 249) might perhaps be applied to the beryllium aluminium solution in caustic soda obtained in the first paragraph of the procedure given above ; it depends on colorimetry of a beryllium lake with p-nitrobenzene-azoorcinol and should be superior to the 8-hydroxyquinoline method.

E. B. Sandell (*Ind. Eng. Chem., Anal. Edn.*, 1940, **12,** 674 ; "Colorimetric Determination of Trace Metals," New York, 1944, pp. 155-156) uses a method based on the fluorescence of a morin lake of beryllium in caustic soda solution which is particularly directed to the determination of traces of beryllium in silicates. By its means he found 0·0005-0·001 per cent. Be in granites, and claims that under such conditions the element can be determined to within ± 0·0001 per cent.

(20) Lithia

In rocks, lithium is usually present only in spectroscopic traces, but, when it is present in small quantity, it is weighed as chloride, together with the chlorides of sodium and potassium, in the standard method for alkalis (p. 84) ; and, whether the potassium is separated as the perchlorate or as the chloroplatinate, lithium passes together with

* *Z. Anal. Chem.*, 1933, **93,** 287.

† *Contributions to Geochemistry*, 1942-45, *U.S. Geol. Surv. Bull.* 950, 1946, 91-100.

sodium into the filtrate. (On the other hand if sodium is determined as sodium zinc uranyl acetate, part of the lithium accompanies the sodium while the remainder will count as potassium.) For the small amounts present in some rocks, non-determination of the lithia, therefore, involves only a very slight additive error in the figure for soda. If there is reason to believe, either from its content of a small amount of a lithium mineral or from the presence of lithium minerals in the near vicinity,* that a rock possibly has a small but weighable lithia content, then it will be sufficiently accurate if the lithia is extracted by an organic solvent from the weighed mixed chlorides, the separation of potassium being carried out last of all. This procedure is described first below.

In the analysis of lithium ores and minerals, or of rocks containing noteworthy amounts of lithium minerals, the position is very different. An appreciable content of lithium chloride renders the mixed chlorides too hydroscopic to weigh. Moreover, owing to the relative insolubility in water of lithium fluoride, oxalate, carbonate, and phosphate, considerable quantities of lithium may be lost if either the normal Lawrence Smith or Berzelius method of isolation of the alkali metals is indiscriminately employed. As a result, when a substantial amount of lithium has to be determined with accuracy, a specially devised procedure for the isolation of the alkali metals, as well as for the separation of the lithium from sodium and potassium, has to be adopted. The procedures for this are described after that of the simple extraction process for small amounts.

(a) Extraction Method for Small Amounts of Lithia

Of the reagents used for extraction, there is little to choose between pyridine and amyl alcohol, according to Hillebrand-Lundell (p. 526); isobutyl alcohol has been claimed to be more efficient.† There is a small correction to be applied in the case of isobutyl alcohol. Pyridine has a disagreeable odour.

* Lithium minerals commonly occur in pegmatites.
† *Analyst*, 1929, **54**, 370.

PROCEDURE.—Whichever solvent is used, the mixed chlorides (after weighing) are dissolved in as little water as possible and transferred without loss to a small flat-bottomed flask. A drop or two of hydrochloric acid is added, the flask is placed on the sand-bath, and the contents evaporated to complete dryness. To prevent condensation and to assist in this operation, the neck of the flask should be wrapped with felt. The flask is then attached to a reflux condenser and boiled with the solvent for ten minutes, after which the contents are filtered in a fritted glass filter funnel, with the aid of some suction, and washed with the solvent. The residue in the filter is dissolved in warm water, collected in a test-tube inside the filter flask, and returned to the small flat-bottomed flask for re-evaporation to dryness, and one or two further extractions. The combined filtrate is evaporated in a small weighed platinum dish on the water-bath, and finally at a low heat over a small flame for a few moments, and the weight of lithium chloride determined.

When pyridine is used, the last of the organic matter is destroyed by means of sulphuric acid, so that after evaporation of the acid the lithium is weighed as sulphate. In fact, owing to the extremely hygroscopic nature of lithium chloride, conversion to sulphate is advisable in any case. The weight of lithium sulphate is re-calculated as lithium chloride and subtracted, together with the KCl equivalent of the $KClO_4$, from the weight of the total chlorides to give NaCl by difference.

A convenient apparatus for the extraction consists of a 50 c.c. conical flask into which is corked a very small double surface condenser the body of which is only 3-4 inches long. The top end of the reflux condenser should be fitted with a calcium chloride tube to prevent ingress of moisture. Two extractions with about 20 c.c. of A.R. pyridine heated over a small luminous flame will suffice for the small amounts of lithia present in most rocks and rock-forming minerals. Owing to its powerful solvent action, pyridine must not be allowed to come into contact with rubber. A cork must therefore be used in the neck of the distillation flask and the fritted glass filter crucible must come below the level of the rubber cap. The use of a standard ground-joint

crucible is a more desirable arrangement.

Opinions are divided as to the comparative efficiency of pyridine and isobutyl alcohol. In either case the solvent has to be absolutely dry, as also the apparatus with which the salts and liquid come into contact. Isobutyl alcohol has to be re-distilled over quicklime before use. Ordinary grades of pyridine should be dried over potassium hydroxide, re-distilled, and the fraction used that boils between 114° and 116° C., though A.R. pyridine, as sold by reputable firms, is guaranteed to give no reaction for water. In view of the precautions which have to be undertaken to insure dryness, and the several evaporations and extractions, the method is rather slow and tedious with risk of loss. Indeed for the highest accuracy it may be as well to run the alkali determinations in duplicate, taking the average of the two weights of combined chlorides, using one lot of salts for lithia and the other for potash.

The main objection to all these extraction methods is the pronounced tendency for lithium chloride to be occluded inside crystals of other alkali chlorides ; also the formation of insoluble lithium hydroxide.

(b) Determination of Substantial Amounts of Lithia

In the following method, which is due to S. Kallmann,* decomposition of the mineral and extraction of the alkalis is achieved by a combination of the Berzelius and the J. Lawrence Smith methods. The sample is treated with hydrofluoric acid and most of the interfering elements are eliminated by precipitation with calcium hydroxide. The fluorine ions are precipitated as calcium fluoride, and the bulk of the lithium is in the aqueous extract. The residue, which invariably occludes some lithium, is then submitted to a modified form of Lawrence Smith fusion. Owing to the fact that the silica has already been largely removed by the initial treatment with hydrofluoric acid, the Lawrence Smith fusion can be carried out at about 700° C., and in a much shorter time than usual. Kallmann claims

* "Determination of Lithium in its Minerals." *Ind. Eng. Chem. Analyt. Edn.*, 1944, **16**, 712-717.

that the aqueous-extracted residue from this fusion is always free from weighable amounts of lithium, and that the method is applicable to all lithium minerals of both silicate and phosphate type (*i.e.*, including amblygonite). He claims that in numerous determinations of lithium in lithium minerals, all residues or precipitates, discarded in the procedure given below were found to be free of weighable amounts of lithium.

Procedure.—Extraction of Alkalis. 0.5 g. of the finely ground sample is weighed into a small platinum dish, moistened with water, 25 c.c. of hydrofluoric acid added, and evaporated to dryness on the water-bath. A further 10 c.c. of hydrofluoric acid are added and the evaporation repeated, the salts being finally dried at about 150° C.

The residue is digested on the water-bath with 25 c.c. of hot water for about five minutes (complete solution is rare when dealing with high-grade lithium minerals). The solution and any residue are completely transferred to a 250 c.c. beaker containing 2 g. of CaO in 75 c.c. of water. (The CaO is prepared by freshly igniting some of the special grade of calcium carbonate used for the Lawrence Smith fusion in the standard method for alkalis.) The contents of the beaker are boiled for about two minutes, and the precipitate allowed to settle a while. The liquid is filtered through a 12 cm. No. 40 Whatman paper into a 400 c.c. beaker, the precipitate being completely transferred to the paper and washed six times with hot water containing calcium hydroxide. Retain the residue. (Residue I).

1 c.c. of ammonia and two half-inch cubes of ammonium carbonate are added to the filtrate, which is then boiled and promptly filtered through a 11 cm. No. 40 Whatman paper. The precipitate (Residue II) is washed with 1 to 50 ammonia containing some ammonium carbonate, and the filtrate retained (Filtrate A).

Residues I and II are ignited in a 30 c.c. platinum crucible. The cooled residue is intimately mixed (in the crucible) with 1 g. of ammonium chloride, the crucible lid placed in position, and the crucible placed in a hole in an asbestos board and heated, gently at first, precisely as described on pp. 80-81, except that the final heating need not be so strong

or so prolonged, the charge being melted or sintered with little difficulty. On cooling, the crucible is immersed in hot water in a 250 c.c. beaker and stood in a warm place for at least six hours. The crucible is removed from the beaker and any of the sinter adhering to the crucible carefully transferred to the beaker. The liquid is heated to boiling and filtered through a 12 cm. Whatman paper into a 400 c.c. beaker, the residue being transferred to the paper and washed six times with hot water containing calcium hydroxide, after which the residue is discarded. The filtrate is subjected to an ammonium carbonate precipitation, filtration and washing as described in the previous paragraph the filtrate (Filtrate B) being retained. The precipitate is washed back into the beaker and dissolved in a few drops of hydrochloric acid. The solution is rendered just ammoniacal, the ammonium carbonate separation repeated, and the liquid filtered through the original paper. Filtrate C thus obtained is retained, and the residue is discarded.

On combining filtrates A, B, and C, all the lithium is now in one solution, which is evaporated to dryness in platinum on the water-bath. The ammonium salts are carefully volatilized as in the standard method for alkalis, and, on cooling, 30 c.c. of hot water are added to dissolve the salts. 4 drops of ammonia and 6 to 8 drops of saturated ammonium oxalate solution are added, the liquid heated to boiling, and then allowed to stand cooling for at least an hour, filtered through a 9 cm. No. 40 Whatman paper, and washed six times with 1 per cent. ammonium oxalate solution. The precipitate is washed back into the original platinum dish, dissolved in a little hydrochloric acid, the ammonium oxalate separation repeated, filtered through the original paper, and the filtrates united. These are then evaporated to dryness in platinum on the water-bath, and the ammonium chloride volatilized as before.

The dry salts are taken up in the platinum dish with about 30 c.c. of hot water and 3 drops of hydrochloric acid, brought carefully to the boil and 10 per cent. barium chloride solution added a drop at a time in quantity sufficient to precipitate any sulphate present. The dish is allowed to stand for at least two hours, filtered through a 7 cm. No. 40 Whatman

er into a 250 c.c. beaker, and washed ten times with water. The filtrate is rendered just ammoniacal, two [-inch cubes of ammonium carbonate added, heated to ing, filtered, and the barium carbonate precipitate washed h dilute ammonia-ammonium carbonate wash liquid. precipitation is repeated, the filtrates united, and the cipitate discarded.

'he combined filtrates are evaporated to dryness in platin, and the ammonium salts carefully volatilized. The s are taken up with 40 c.c. of water in the platinum dish small additions of ammonia, ammonium carbonate, ammonium oxalate made dropwise. The liquid is efully brought to boiling point and allowed to stand for least two hours before being filtered through a 7 cm. 40 Whatman paper, and washed with dilute ammonia-monium carbonate solution. The precipitate is dis-ved in hydrochloric acid and the precipitation repeated, final precipitate being discarded.

'he combined filtrates are evaporated to dryness in plat-n and the ammonium salts volatilized. The salts are istened with hydrochloric acid, again evaporated to ness, and once more heated, this time to dull redness a moment, to remove any traces of ammonium salts.

Separation of Lithium from Potassium

Kallmann (*op. cit. supra*) shows that the separation of ium from potassium by the n-butyl alcohol-HCl method very satisfactory; he also revised Willard & Smith's hod* and extended it to the separation of lithium from h sodium and potassium. Anhydrous n-butyl alcohol sufficient purity is now on the market.

'ROCEDURE.—**The mixed chlorides, obtained as described ve, are dissolved in a little water, 5 c.c. of perchloric l added, and evaporated to dryness on a sand-bath or plate at a temperature not exceeding 350° C.**

0 c.c. of anhydrous n-butyl alcohol and 0·2 c.c. of per-oric acid are added to the mixed perchlorates, the solution heated to boiling (the B.P. of n-butyl alcohol is 116° C.),

'. *Am. Chem. Soc.*, 1922, **44**, 2816.

and 8 c.c. of a 20 per cent. solution of hydrochloric acid in n-butyl alcohol are added, commencing with a drop at a time, while the mixture is constantly stirred. On cooling to room temperature, the precipitate (consisting of sodium chloride and a mixture of potassium chloride and potassium perchlorate) is collected on a fritted-glass filter crucible and washed about eight times with a 6 per cent. solution of hydrochloric acid in n-butyl alcohol. The filter crucible and its residue are retained if soda and potash are to be determined.

The filtrate and washings, which have been received in a platinum dish of about 250 c.c. capacity, are diluted with one-third their volume of water when the whole separates out into two layers, the lithium chloride and perchlorate being in the aqueous layer. The whole is then evaporated to complete dryness on the water-bath. 10 c.c. of water, 5 c.c. of nitric acid, 3 c.c. of perchloric acid, and 1 c.c. of sulphuric acid are added and the mixture evaporated on a sand-bath to strong fumes of sulphuric acid. This treatment usually suffices to destroy any brown coloration due to organic matter, but, if not, a few drops of nitric acid should be added and the fuming continued. The excess of sulphuric acid is finally fumed off. After cooling, 15 c.c. of water are added, the contents brought into solution on the water-bath and then transferred to a small, ignited and weighed, platinum dish, in which they are evaporated as far as possible on the water-bath. The platinum dish is then carefully heated over a small bunsen flame until all acid has been expelled, and concluding by just bringing it to a dull red heat for a moment or two. The lithium so obtained is then weighed.

The residue on the glass filter-crucible is dissolved in hot water and sodium separated from potassium by the standard method of pp. 85-86.

It is desirable to determine a correction for the solubility of the three alkali chlorides in the 6 per cent. solution of hydrochloric acid in *n*-butyl alcohol and a blank for all the reagents used. It is fortunate that caesium and rubidium are rarely encountered in lithium minerals, with the exception of lepidolite, but even that mineral usually

contains these two metals in such small amount that no special provision for their occurrence need be considered.

(21) Determination of Copper, Zinc, and Lead

Normally these metals are present in rocks only in extremely small quantity, but in mineralized regions the content of any of these metals may rise appreciably. The metals may be present as the sulphide ores or their oxidized forms such as sulphates, carbonates, or oxides, in which case they can be extracted from the powdered sample by ordinary acid leaching (without hydrofluoric acid). On the other hand one or more of these metals may enter the crystal structure of certain of the rock-forming silicates, when they can be got into solution only by fluxes or by the use of hydrofluoric acid. The mineralogical location or the relative mineralogical location of these elements is of value in geochemical studies. Moreover, nowadays more examples are coming to light of the existence of lead-zinc ores in particular, in small quantity and of either detrital or syngenetic origin, in various sedimentary horizons.

In the past the determination of minute quantities of these metals in rocks was perforce restricted to the acid leaching of comparatively large samples, evaporation of the extract, and application of normal inorganic methods of separation. Special organic reagents, however, have increased the range of possibilities ; a colorimetric method for copper using sodium dithiocarbamate has been given on pp. 143-144 ; dithizone (diphenylthiocarbazone, phenylazothionoformic acid phenylhydrazide) introduces the possibility of simultaneously extracting minute quantities of copper, zinc, and lead. The method described by E. B. Sandell* is based on the investigations of Hellmut Fischer and others on the use of dithizone for determining traces of heavy metals.

The sample is decomposed with a mixture of hydrofluoric and perchloric acids. The insoluble residue from this will, particularly if it contains barium sulphate, hold most of the lead that was present in the sample. It is therefore sub-

* *Ind. Eng. Chem. Analyt. Edn.*, 1937, **9**, 464-469.

mitted to a sodium carbonate fusion, and the melt leached with water and filtered; the washed residue is treated with hydrofluoric and perchloric acids to remove any silica remaining, and is finally dissolved in hydrochloric acid. The three solutions so obtained are extracted separately with a carbon tetrachloride solution of dithizone in a citrate solution containing a slight excess of ammonia (pH approximately 8.5), the major constituents of the rock remaining in the aqueous phase.

When the carbon tetrachloride layer is separated and shaken with 0·01 N HCl, the dithizonates of zinc and lead are decomposed, giving the chlorides of these metals in the aqueous phase. The copper complex is not decomposed by the dilute acid and remains in the carbon tetrachloride, which is evaporated to dryness and the residue ignited to cupric oxide.

Sandell re-dissolves this in hydrochloric acid and determines the copper by extractive titration with dithizone-carbon tetrachloride at a pH of approximately 3·5 or by mixed-colour colorimetry with the same reagent in acid solution. The 0·1 N HCl solution containing the lead and zinc is made up to volume and the two metals are determined colorimetrically in separate aliquots with dithizone; zinc by the mixed colour technique at a pH of about 4.1 in the presence of thiosulphate to prevent the interference of lead, and lead in an ammoniacal solution containing potassium cyanide to prevent the reaction of zinc. For the operative details the original paper should be consulted; it shows that the method is capable of determining minute amounts of the three metals in rocks with accuracy to three of four places of decimals of one per cent.

Sandell has extended this method to include also nickel, cobalt, and cadmium (*Ind. Eng. Chem. Anal. Edn.*, 1939, **11**, 309 and 364).

CHAPTER VII

SPECIAL METHODS

A. FOR SOME CONSTITUENTS UNDER SPECIAL CONDITIONS

1. Hydroxyquinolinolate Method for Magnesia.

The filtrates from the calcium oxalate are, if necessary, evaporated down to 300 c.c., rendered very slightly acid with hydrochloric acid, then heated to 60-70° C. A higher temperature must be avoided or a tarry rather than crystalline precipitate will be obtained subsequently. The solution should contain sufficient ammonium salts to prevent precipitation of the hydroxide, but if present in large amount and little magnesia is expected, they should first be destroyed (see p. 66).

10 c.c. of a 5 per cent. solution of 8-hydroxyquinoline in $2N$ acetic acid are then added, and diluted ammonia (1 : 1) is added drop by drop, with stirring, from a tap-funnel, until the solution is distinctly alkaline, when a bulky white crystalline precipitate settles out. A yellow colour in the liquid indicates that an excess of the reagent was added. As soon as the precipitate has settled, it may be filtered in a Munroe crucible or fritted glass filter, washed with hot dilute ammonia (1 : 40), dried at 130-140° C. for forty-five minutes, and weighed as $Mg(C_9H_6ON)_2$. An even more rapid method is titration of the hydrochloric acid solution of the precipitate with potassium bromate-potassium bromide solution, but this is scarcely accurate enough for scientific purposes.

It should be noted that in this, and in all precipitations by 8-hydroxyquinoline, it is highly desirable to know fairly closely the amount of the precipitant required, as this reagent is not very soluble in water. The excess should not be more than 1 c.c. of 5 per cent. solution per 100 c.c. of final solution. If more is added, solution and re-precipitation may be necessary to get rid of excess reagent.

If preferred, the precipitate may be filtered on paper, washed with hot dilute ammonia, and ignited in a platinum crucible to MgO. The ignition should be commenced slowly. This method is preferred by the author to that of weighing the magnesium as oxyquinolate. Moreover, it has the advantage that, if it is desired to determine the manganese precipitated with the magnesia, the precipitate can be dissolved directly in dilute sulphuric acid and the manganese determined colorimetrically, whereas the organic matter in the oxyquinolate has to be destroyed with sulphuric and nitric acids before this can be done.

(2) Colorimetric Method for Fluorine.

The indirect method of Steiger,* as modified by Merwin,† is more rapid and accurate than the gravimetric method when the amount of fluorine is known to be small, but it is not suitable for large amounts. It is specially recommended in cases where the fluorine content is expected to be less than 0·25 per cent. The method is based on the fact that fluorine has a marked bleaching effect, even when present in small quantities, on the colour produced when a titanium solution is added to hydrogen peroxide. But this coloration is also affected by sodium salts, sulphuric acid, and by temperature. The conditions have thus to be standardized and the results referred to the diagram constructed by Merwin.

Procedure.—**2 g. of the powdered sample are fused with a mixture of 4 g. each of sodium and potassium carbonates or 7 g. of sodium carbonate (weighed out to within a few mg.), leached, filtered, and washed. Instead of adding 3-4 g. ammonium carbonate in order to precipitate silica, alumina, and ferric oxide, as is usually done, an improvement is to use 20 c.c. of the special zinc nitrate solution (p. 12). The tedious destruction of ammonium carbonate is thus obviated. Vanadium (which gives a brown coloration with hydrogen peroxide in acid solution) should next be removed as follows: Dilute sulphuric acid is carefully added until the solution is just neutral, as shown by spotting**

* *J. Am. Chem. Soc.*, 1908, **30**, 219.
† *Am. J. Sci.*, 1909, **28**, 119.

with a thin stirring rod on to a methyl red paper. 0·1 g. of silver sulphate is added, and the solution allowed to stand several hours, after which A.R. sodium chloride is added in excess, and the liquid filtered. The filtrate is then reduced by evaporation to about 75 c.c., 3 or 4 c.c. of hydrogen peroxide added, followed by 10 c.c. of standard titania solution (containing 0·01 g. TiO_2 ; see p. 14), when the characteristic yellow coloration appears. 3 c.c. of concentrated sulphuric acid are added from a 10 c.c. burette and the solution made up to 100 c.c. at a temperature of about 22° C. in a Nessler

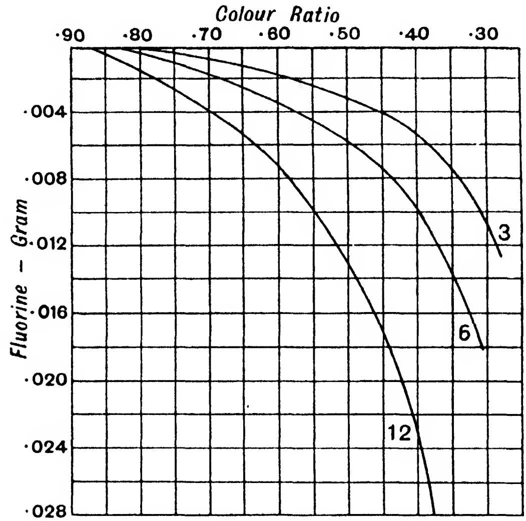


FIG. 11.—MERWIN'S DIAGRAM FOR FLUORINE.

$$\text{Colour ratio} = \frac{\text{depth of standard solution}}{\text{depth of test solution}}.$$

Each solution is peroxidized and made up to 100 c.c. and contains 0·01 g. of TiO_2. The test solution contains the number of c.c. of concentrated H_2SO_4 indicated by the numbers near the curves, and the amounts of fluorine shown, besides sulphates equivalent to 4 g. each of Na_2CO_3 and K_2CO_3. The standard solution contains an indefinite amount of acid between 3 and 5 c.c. The chart was made at 22° C., but it is not significantly different at any temperature between 19° and 25° if both solutions are at the same temperature. If the test solution is 5° warmer than the standard the curves are displaced toward the left hand about 0·02 for 12 c.c. of acid, and 0·01 for 3 c.c. of acid. The total colour of the solutions is not significantly affected by 10 per cent. change of water content. (Reproduced by permission from *U.S. Geol. Survey Bull.* 700.)

cylinder painted as described on p. 74. To 10 c.c. of standard titania solution containing 0·01 g. TiO_2, 4 c.c. of hydrogen peroxide are added and 3 c.c. of concentrated sulphuric acid and the volume made up to 100 c.c. After mixing, this solution is slowly run into a second blackened Nessler cylinder until the depth of liquid is such that, on comparing the two tubes on light transmitted up the columns by reflection from a white tile below, the absorption of light is the same in each. The volume of liquid run in from the burette is measured. The colour ratio is then equal to the volume of the standard solution used divided by the volume of the test solution (100 c.c.). By referring the colour ratio to Merwin's diagram (Fig. 11) for the standard conditions here given, the weight of fluorine present in the test solution is read off. The colour ratio must be greater than 0·40 before the amount of fluorine can be read accurately. If the colour ratio is smaller (indicating more fluorine), more sulphuric acid should be added and a new colour comparison made. Merwin's diagram gives curves corresponding to the addition of 3, 6, and 12 c.c. of acid which should cover all cases. Those whose working conditions do not allow of the 22° C. should construct curves to suit their particular conditions.

(3) Test for Barium and Strontium, and Direct Determination of Lime, and Magnesia

In the first edition of this book a method was given for the direct determination of lime and/or magnesia based on initial decomposition of the rock by a mixture of hydrofluoric and perchloric acids. It was remarked, however, that when much lime was present difficulty was experienced in achieving complete decomposition. The method therefore was recommended as being suitable only to felspars, glasses, and rocks containing not more than about 7 per cent. lime. More recently it has been shown that, by increasing the amount of perchloric and hydrofluoric acid some two to threefold, complete decomposition appears to be generally achieved.* Moreover, G. H. Osborn† has

* G. G. Marvin and L. B. Woolaver. *Ind. Eng. Chem.* (*Anal. Ed.*), 1945, **17**, 554-556. † G. H. Osborn. *Mineralog. Mag.*, 1946, **27**, 259 and 262.

carried the matter a stage or two further. Finding that calcium sulphate is entirely soluble in perchloric acid, but that while barium and strontium sulphates are also soluble they are completely precipitated on the addition of sufficient sulphuric acid, he affords us a ready test for barium, and a method of removing barium and strontium before precipitation of lime and magnesia should the quantities of barium and strontium ever be so considerable as to make this desirable.* He further shows that, by precipitating calcium as the oxalate in acetic acid, calcium may be precipitated directly without the necessity to remove the R_2O_3 group by ammonia.

PROCEDURE.—(*a*) **1 g. of the powdered sample is weighed into a small platinum dish, 20 c.c. of perchloric acid (60 per cent.) and 10 c.c. of hydrofluoric acid are added, and the solution evaporated to dryness on a sand-bath in a fume cupboard. A further 20 c.c. of perchloric and 10 c.c. of hydrofluoric acid are added and the mixture once more evaporated to dryness. The residue is then treated with 20 c.c. of perchloric acid until salts begin to crystallize out. The contents of the dish are then digested with water over the water-bath for a few minutes, and then washed into a beaker and diluted to 200 c.c. with boiling water.**

(*b*) *Tests for Barium and Strontium*

To the solution, which should be perfectly clear if decomposition has been complete, or unless barium sulphate is already present, 1 c.c. of sulphuric acid is added. An immediate precipitate is indicative of barium, but unfortunately barium cannot be determined in this way unless strontium is entirely absent, for, if both elements are present, as is so often the case in rocks, the barium will co-precipitate most of the strontium under these conditions. If, however, 10 c.c. of 1:1 sulphuric acid be added and the liquid evaporated to 100 c.c., the whole of the barium and strontium will be precipitated. The absence of a precipitate at this stage (after standing) is not conclusive evidence of the absence

* Normally, in the absence of sulphates, strontium is mainly precipitated as oxalate with lime, while barium is thrown down with the magnesium ammonium phosphate.

of strontium, but, if there was also no precipitate when the 1 c.c. of sulphuric acid was added, above, then the absence of both barium and strontium is indicated.

(c) Direct Determination of Lime without prior Removal of R_2O_3; Magnesia not required

Whether or not sulphuric acid has been added to test for barium and strontium in the previous paragraph, the liquid (diluted, if necessary, to 200 c.c.) is made just ammoniacal, 20 c.c. of glacial acetic acid added, brought to the boil and 2 g. of ammonium oxalate added. After standing for at least four hours — overnight if the amount of lime is very small — the precipitate of calcium oxalate is removed, washed free from acid with 0·1 per cent. ammonium oxalate solution, ignited, and weighed as CaO.

(d) Direct Determination of Lime and Magnesia

The material is brought into solution by method (*a*), 5 c.c. of concentrated hydrochloric acid are added, when the usual brown coloration due to iron appears. A double ammonia precipitation is then carried out, each precipitate being washed three times with hot 2½ per cent. ammonium chloride solution, but the tedious washing with ammonium nitrate is omitted, unless the R_2O_3 figure is required.

The solution is acidified, evaporated to a suitable bulk (usually 200-300 c.c.), and lime precipitated in the usual way as calcium oxalate, which is ignited and weighed as CaO.

Magnesia can be precipitated from the calcium oxalate filtrate either as magnesium ammonium phosphate or, more rapidly, by means of 8-hydroxyquinoline. For the rapid precipitation by 8-hydroxyquinoline of slightly larger amounts of magnesia, as in the analysis of cement, etc., J. C. Redmond and H. A. Bright* recommend that the solution should have a volume of about 350 c.c. and, after heating to the usual temperature of 60-70° C., 20 c.c. of 8-hydroxyquinoline solution are added (prepared by dissolving 25 g. of the compound in 60 c.c. of glacial acetic acid and diluting to 2 litres with cold water; 1 c.c. is equivalent to 0·0016 g. of MgO).

* *Bureau of Standards J. Research*, 1931, **6**, 113-120.

This is followed by the addition of 4 c.c. of strong ammonia (sp. gr. 0·9) for each 100 c.c. of solution; the whole is stirred mechanically for ten to fifteen minutes and then allowed to stand until the precipitate has settled. The precipitate is dealt with as described on p. 159. If no stirrer is available, the ammonia is added first.

(4) Direct Determination of Baria and Strontia.

The following method for the determination of baria and strontia is the most accurate one avilable* but takes rather longer to carry out than the methods described on pp. 106 and 64. However, when baria and strontia only are required, or if the decision to determine them is made after the lime and manganese residues have been discarded, then the following method may be adopted. Greater accuracy may be gained by taking 2 or 3 g. of sample when it is known that there are only small amounts present of the constituents sought.

Procedure.—**If a silicate, the sample is decomposed with a mixture of hydrofluoric and sulphuric acids. A carbonate or other acid-soluble mineral, is dissolved in hydrochloric or nitric acid, but the solution should be neutral or only slightly acid before the addition of a tenfold excess of dilute sulphuric acid and then four volumes of alcohol. The mixture is stirred and allowed to stand overnight. It is then filtered through a double No. 40 paper, and washed with 75 per cent. alcohol. The paper is incinerated in platinum and ignited to dull redness. The sulphates are next fused with sufficient A.R. sodium carbonate to convert them to carbonate, the melt leached with water, filtered through a No. 40 paper, and washed with dilute sodium carbonate solution until free from all traces of sulphate. The precipitate is dissolved in dilute nitric acid on the paper, filtered into a 100 c.c. beaker, and well washed. The solution is evaporated on the sand-bath to absolute dryness. Lime is removed by nitric acid according to Rawson's method (see p. 64). The residue of barium and strontium nitrates on the glass filter-crucible is washed ten times with the special nitric acid to insure the complete removal of lime.**

* This is superior to the oxalate method as regards completeness of the precipitation of strontium.

An aqueous solution of the residual nitrates is made (as described on p. 65), and from this baria is removed and weighed as chromate, strontia being determined in the filtrate.

Baria.—In case there is still some lime present, the small amount of nitric acid is neutralized with a few drops of ammonia and then, using methyl red, the solution is acidified with a few drops of acetic acid. This prevents co-precipitation of lime. 10 c.c. of ammonium acetate solution (300 g. per litre and neutralized by ammonia) are added, the liquid boiled and, while swirling, 5 c.c. of ammonium bichromate free from sulphuric acid (100 g. per litre) are slowly poured in. After allowing to settle and cool, the clear liquid is decanted through a double 40 paper, and the precipitate of barium chromate is washed with ammonium acetate (20 c.c. of the stronger solution diluted to 1 litre) until the filtrate is no longer coloured by the bichromate solution. The precipitate is ignited and weighed as barium chromate. If any greenish spots appear, due to reduction of the chromate, these will re-oxidize on continued ignition.

The 5 c.c. of ammonium bichromate solution of the strength indicated is suitable for the precipitation of the equivalent of 0·135 g. of BaO. It should be adjusted to the amount of barium anticipated.

Strontia.—After the addition of a little nitric acid, the filtrate from the barium chromate is evaporated to a small volume and the strontia precipitated by a decidedly ammoniacal solution of ammonium carbonate, filtered on a 40 paper, and washed with a little hot water. The precipitate is dissolved on the paper in the minimum amount of hydrochloric acid and the paper washed. Chromium should have been removed in solution by the ammonia. If any still remains, the solution will now be violet or green, but this chromium will be removed by the final washing of the strontium sulphate. A few drops of 1 : 1 sulphuric acid (more if much strontia is expected) are added and the solution evaporated to a small bulk, an equal volume of alcohol added, and allowed to stand overnight. Next morning the strontium sulphate is filtered on a small 40 paper, ignited, and weighed. If spectroscopic examination reveals admixture with appreciable lime, the

latter can be removed by fusion with sodium carbonate, filtering, conversion to dried nitrates, and the nitric acid separation repeated.

(5) Determination of Silica in Presence of Fluorine.

When the content of fluorine exceeds 2 per cent., the ordinary method for the silica determination is liable to give low results on account of the loss of some silica as volatile silicon tetrafluoride during the evaporation with acid. In such cases silica is determined on the residues from the fluorine determination as follows :

Procedure.—The residue after extraction of the melt, together with the precipitates thrown down by the zinc nitrate and zinc oxide solutions, is transferred as completely as possible by means of the wash-bottle to a large platinum dish. The papers are well washed with water containing some hydrochloric acid, and the washings added to the liquid in the dish, which is acidified with an excess of strong hydrochloric acid and evaporated to dryness. Silica is then determined in the usual way (see p. 53), two recoveries being made.

(6) Determination of Manganese when present in Quantity ; Also when Accompanied by Substantial Amounts of Nickel, Cobalt, Copper, or Zinc

In the analysis of manganese-rich silicates such as spessartite, rhodonite, tephroite, piedmontite, etc., or of rocks containing appreciable amounts of these minerals, considerable quantities of manganese are encountered, and, when the analysis of oxide ores of manganese is undertaken, even more substantial quantities of manganese have to be handled. Not only in all of these cases, but whenever manganese exceeds one or two per cent. the colorimetric method is inadvisable as the greatly increasing dilution required rapidly reduces the accuracy obtainable. Moreover, although 40 c.c. of saturated bromine water will precipitate 50 mg. of MnO with the ammonia precipitate, doubt as to the composition of the ignited residue will cause increasing error with a substantial manganese content. Further, if considerable quantities of MnO are

precipitated with the R_2O_3, some magnesium is almost invariably carried down (possibly as $MgMn_2O_4$).

The analyst then has the choice between a number of separations according to which elements in the above heading are present and in what proportions.

If any of these elements are present in some quantity, it has been usual in the past to recommend the basic acetate separation and this is described in Procedure (*a*) below. By this method the iron and alumina are precipitated while the other metals pass into the filtrate, from which they are precipitated (together with any platinum) by means of ammonium sulphide. The basic acetate separation is undeniably tricky and requires to be carried out with great care. It certainly introduces much non-volatile sodium acetate, and, in the presence of much cobalt especially, the separation may be far from perfect. Provided these drawbacks are not overlooked, this old-established method may prove useful on occasion, but it should be regarded as the poorest of the separations here presented.

For analyses of the highest accuracy, there is much to be said in some cases for double precipitation with ammonia in the usual way (without bromine), and determining the amounts of manganese, nickel, cobalt or copper carried down with the ammonium precipitate (the necessary correction being made on the alumina), for such of these metals as may be present are readily determined on an aliquot of the solution, resulting from a pyrosulphate fusion, by the periodate colorimetric, the dimethylglyoxime, the α-nitroso-β-naphthol, and a colorimetric method respectively. In this way, and perhaps in this way only, is the highest accuracy for the alumina figure maintained, the main fractions of the manganese, nickel, cobalt or copper being determined on the combined filtrates from the double ammonia precipitation. Indeed, whichever separation is used, the R_2O_3 precipitate requires checking for Mn, Ni, Co, and Cu.

If manganese is the only one of these metals present in quantity, it may then be precipitated as sulphide in the combined filtrates from the double ammonia precipitation and thereafter determined by the bismuthate method described on p. 172 (or gravimetrically as phosphate, p. 174).

On the other hand, manganese sulphide is not a nice precipitate to handle, and, if large amounts of manganese are left together with lime and magnesia, the troubles caused by trying to filter a big manganese sulphide precipitate may be serious ; yet such a situation may sometimes be unavoidable. Probably the best method of all when manganese is present in considerable amounts is to precipitate it as the dioxide by potassium chlorate in nitric acid. The separation (given on pp. 173-175) is not perfect ; but the precipitated manganese dioxide can be dissolved and all contaminating iron or aluminium precipitated from this solution by ammonia (or hexamine) without appreciable manganese being carried down, and conversely, if the filtrates for the bulk of the dioxide are treated in the usual way, the manganese left in them is readily recovered. This scheme may seem a little complicated, but in practice it is actually a good clean procedure when manganese-high minerals are involved. From the combined manganese precipitates, after re-solution, the manganese is best precipitated as phosphate and weighed as $Mn_2P_2O_7$.

For nickel minerals it should be remembered that Harwood and Theobald's dimethylglyoxime method serves for quite considerable amounts.

The separation of the sulphides of manganese and zinc from those of nickel, cobalt, and copper by dilute acid is not particularly good. Mixtures of these metals need a good deal of care and the best method in a particular case depends greatly on the proportions.

If much manganese is accompanied by iron and alumina, but no nickel, cobalt, etc., hexamethylene tetramine will precipitate the iron and alumina with a minimum contamination by manganese. Under these conditions it gives a cleaner separation than with ammonia, but sulphate must be present, and zinc and nickel co-precipitate badly (*Zeit. Anal. Chem.*, **78,** 133). It is not such a good separation as the chloric acid method.

The basic acetate separation detailed below takes the place of the ordinary ammonia precipitation of iron, alumina, etc.

(a) *Basic Acetate Separation*

PROCEDURE.—A strong solution of sodium carbonate is cautiously added to the filtrate from the silica until the liquid turns a dark red and there is a slight turbidity which cannot be dispelled by stirring. The volume of the liquid should be about 200 c.c. and a clock glass should be used to prevent loss by effervescence. The effervescence caught on the clock glass is then rinsed back into the beaker and dilute hydrochloric acid is added drop by drop, very cautiously and with constant stirring, until the turbidity just disappears but the liquid is still dark red. It is essential that no excess of acid be used for this operation, otherwise acetic acid will subsequently be formed in amount sufficient to render the precipitation of basic acetates of iron and aluminium incomplete. If the analyst overshoots the mark, however, the operation can easily be repeated.

1-3 g. of sodium acetate dissolved in a little water are then added, the amount depending on the combined content of iron and alumina expected. The liquid is diluted to 300 c.c., or 350 c.c. if 3 g. of sodium acetate are used, and heated to boiling for *one minute only*. The precipitate of basic acetates is allowed to settle for a few minutes, filtered through a No. 41 paper and washed two or three times with hot water containing a little sodium acetate. The precipitate is then dissolved in hydrochloric acid and re-precipitated with ammonia. A second precipitation with ammonia may be carried out when conditions require it. The ammonia precipitate is washed with ammonium chloride and ammonium nitrate in the usual way and ignited to R_2O_3. The final filtrate is reserved for the determination of lime and magnesia.

The filtrate from the basic acetate separation contains the manganese and any nickel or cobalt, but there is invariably sufficient iron and alumina still present to warrant their recovery. The filtrate is accordingly made just alkaline with ammonia and evaporated to about 100 c.c. Ammonia is added from time to time to keep the liquid just alkaline, and the small precipitate is filtered, washed, and added to the main ammonia precipitate. The filtrate is caught in a small flask, and if the platinum dish is stained brown by manganese,

this is removed in a few drops of hydrochloric acid containing a drop or two of sulphurous acid and added to the filtrate.

The filtrate is made decidedly ammoniacal and saturated with hydrogen sulphide when manganese is precipitated as the sulphide. Nickel, cobalt, copper, and zinc, if present, as well as any platinum derived from the apparatus, are also precipitated at this point. The sulphides are collected on a small filter, washed with ammoniacal ammonium chloride saturated with hydrogen sulphide, and then treated on the paper in a few c.c. of hydrogen sulphide water containing one-fifth of its bulk of hydrochloric acid and washed. The filtrate contains manganese (and zinc) in solution.

The filtrate is evaporated to dryness in a small porcelain dish, a few drops of sodium carbonate solution added, and the liquid again evaporated to dryness to destroy ammonium salts which retard the complete precipitation of manganese. About 10 c.c. of water containing a few drops of hydrochloric acid are used to dissolve the residue, and the manganese is precipitated with sodium carbonate. The manganese carbonate is collected on a filter, washed with water, and ignited in platinum to Mn_3O_4.

The black residue of sulphides on the filter may contain nickel, cobalt, copper, and platinum. In the absence of copper, the sulphides of nickel and cobalt may be dissolved in hydrochloric acid containing a few drops of A.R. bromine, filtered, and evaporated to dryness to remove the bromine. Nickel may be determined by the dimethylglyoxime method and cobalt by α-nitroso-β-naphthol in the presence of each other.

If the bismuthate method is adopted, it is of course essential that the R_2O_3 be precipitated without bromine so that as far as is possible the manganese goes into the filtrate. It is also desirable that the R_2O_3 precipitate after weighing, should be taken into solution by means of a pyrosulphate fusion, oxidized by periodate and a colorimetric determination of the manganese content executed (an aliquot part as small as one-tenth will usually suffice), the necessary correction (calculated as Mn_3O_4) to the Al_2O_3 and MnO figures being made. With manganese present as a main constituent this should also be done.

The bismuthate method consists of oxidizing bivalent manganese to permanganic acid by means of sodium bismuthate in nitric acid, filtering, adding a measured excess of ferrous sulphate and determining this excess by titration with permanganate.

(b) *Separation of Manganese as Sulphide and Determination by the Bismuthate Method*

Ammonium sulphide alone precipitates manganese, zinc, nickel, and cobalt sulphides very imperfectly, but when ammonium chloride is present in quantity, as it is in the filtrates from the ammonia precipitation, precipitation of these sulphides is practically complete. If free ammonia is present, precipitation of Mn and Ni sulphides is retarded. If appreciable quantities of lime, magnesia, barium, or strontium are present, as is usually the case, the ammonium sulphide precipitation is carried out in the cold, as described below.

To the combined filtrates from the double R_2O_3 precipitation is added 2 c.c. of ammonium hydroxide and the liquid placed in a suitable sized conical flask. Sulphuretted hydrogen is passed through to saturation. A further 2 c.c. of ammonium hydroxide is added, and then recently boiled and cooled water added until the level is well up the neck of the flask, which is then stoppered and allowed to stand overnight. Filtration is carried out as expeditiously as possible through paper, and the residue washed with cold 2 per cent. ammonium chloride solution containing a little ammonium sulphide. Reserve the filtrate for the determination of lime and magnesia.

A 22 per cent. solution of nitric acid, *i.e.*, a solution with a sp. gr. of 1·135, is prepared, and the sulphide residue removed from the filter paper and dissolved in it. The filter paper is also washed with several small quantities of the acid and the filtrates collected in the main solution. Further nitric acid of the same strength is added until the volume of the solution, as far as can be judged or anticipated, corresponds to roughly 100 c.c. for each 0·05 g. of Mn present. The solution is cooled to between 10 and 20° C. in a glass stoppered flask. Add 0·26 g. of sodium bismuthate for

each 0·1 g. of Mn anticipated, shake well for one minute, dilute with an equal volume of cold water, filter through fritted glass, and wash the residue well with cool 3 per cent. nitric acid until it is seen to be free from permanganic acid. Ferrous sulphate is then added either as a standard solution or as weighed portions of ferrous ammonium sulphate in amount estimated to require about 10 c.c. of permanganate in the back titration. The liquid is stirred until the permanganic acid is decolorized and, if ferrous ammonium sulphate has been added, until all the crystals are dissolved, and titrate with decinormal potassium permanganate.

A blank determination reproducing all the steps of the method with the same amounts of reagents should be run. The difference between the first titration and that obtained in the blank is the permanganate equivalent of the permanganic acid formed by the bismuthate. It follows that the MnO content of the sample is the same as for this amount of permanganate solution.

L. Lund* has developed a colorimetric method for silicates with 0·5 per cent. or more of manganese. In the solution Mn^{2+} is oxidized to Mn^{7} with $K_2S_2O_8$ and $HgNO_3$ as catalyser, and HPO_4 added to make the oxidizing process irreversible. Mn^{7+} is then titrated with $FeSO_4$, using diphenylamine as indicator with the sharp colour change dark-blue-violet to light green.

PROCEDURE.—(c) *Separation of Manganese by Precipitation as Dioxide, and Gravimetric Estimation by the Pyrophosphate Method*

For this method it is desirable that the solution should contain no other acid than nitric and should be evaporated to a syrupy consistency. 100 c.c. of nitric acid are added, and the solution kept carefully covered in a beaker while it is first boiled for a few minutes to expel oxides of nitrogen and then 5 g. of potassium chlorate are added gradually, in very small quantities at a time. The boiling is then continued until the volume has been reduced to approximately 25 c.c. The cover glass and sides are washed down with a small jet of water, 40 c.c. of cold water added, the

* *Norsk. Geol. Tidsskrift*, 1942, 21, 268-271.

liquid cooled quickly and filtered, preferably through fritted glass, and the precipitate washed with small amounts of cool, colourless nitric acid, and finally ice-cold water retaining the filtrate and washings. (If a supply of chloric acid is available, it can be used with advantage in place of the potassium chlorate, thus obviating the introduction of potassium salts.)

The small amount of manganese contained in the filtrate and washings is recovered and added to the principal manganese precipitate, which is then returned to the beaker in which the precipitation was made and is purified as follows: The precipitate is dissolved in a small quantity of strong sulphurous acid (10-40 c.c.), filtered, washed with hot water, and 2-3 c.c. of hydrochloric acid added to the filtrate, which is then heated until sulphur dioxide is completely expelled. Sufficient bromine water is added to colour the solution strongly, and the liquid then boiled to expel all free bromine. An ammonia precipitation (p. 58) is then carried out, the precipitate washed two or three times with hot water and the filtrate reserved. The precipitate is dissolved in hot dilute hydrochloric acid (1 : 3) and the ammonia precipitation and washing repeated, the filtrate being added to the previous one and reserved. The combined filtrates are acidulated with acetic acid, heated to boiling, and a current of hydrogen sulphide passed through for 10-15 minutes. After standing in a warm place for 15 minutes, the liquid is filtered, and washed with hydrogen sulphide water acidulated with acetic acid and containing a little ammonium chloride. The filtrate now contains all the manganese and is ready for gravimetric estimation by the pyrophosphate method which follows.

The volume of the solution should be adjusted so that it contains not more than 1 mg. of manganese per c.c., and it is acidified with a little hydrochloric acid. 20 g. of ammonium chloride are added and 1-2 g. of diammonium phosphate. The liquid is brought to the boil, and, if necessary, is cleared with hydrochloric acid. Dilute ammonia is then added drop by drop with continuous stirring. The addition of ammonia is stopped when the first precipitate appears, but the stirring and boiling are continued until

the precipitate becomes crystalline. Another drop of ammonia is added and a further pause made for the precipitate to become crystalline whilst stirring. This process is continued until no more precipitate is produced and its silky appearance remains unchanged. 0·5 c.c. of ammonia in excess is then added, and the liquid cooled, preferably in ice water. After standing for 2-3 hours, the precipitate is filtered off, and washed free from chlorides with a faintly ammoniacal 10 per cent. solution of ammonium nitrate. It is ignited, taking the same precautions as for $Mg_2P_2O_7$ (see p. 68), the ignition, however, being completed at 1,000° C., and the residue weighed as $Mg_2P_2O_7$.

(7) Determination of the Higher Oxides of Manganese

In oxidized manganese ores it is usual to encounter MnO_2 in pyrolusite, psilomelane, and wad. Likewise Mn_2O_3 occurs in braunite, and in manganite. Both these oxides may be present in addition to MnO. Mn_2O_3 also enters into the composition of certain silicates, *e.g.*, the manganese epidote known as piedmontite. Some reference to the interference of manganese dioxide with the estimation of ferrous iron has been made on p. 90; likewise the presence of ferrous iron interferes with the determination of the higher oxides of manganese. Mellor* (1913, pp. 381-382) pointed out than in the analysis of highly oxidized manganese ores, completely soluble in sulphuric acid, MnO_2 and Mn_2O_3 can be estimated in the presence of MnO by means of their oxidation of standard oxalic acid solution *but FeO must be absent.* It is probable that even an approximation to such a situation is not common in rocks and minerals. In the presence of FeO an MnO_2 determination will be low in proportion to the amount of FeO present. If MnO_2 were present, the amount of FeO would be correspondingly increased and the Fe_2O_3 decreased; but once the FeO content exceeds the MnO_2, as is very likely to happen, then it is impossible to determine the MnO_2 chemically. The most that can be done when MnO_2 is in excess of FeO is to determine that excess. As is explained and stressed on

* J. W. Mellor. "A Treatise on Quantitative Inorganic Analysis." 1st *Edition., London,* 1913.

p. 90, all that the chemist is doing in such circumstances is to determine the net state of oxidation. The oxalic acid method is probably not too safe for manganic minerals such as piedmontite. The Pratt method (HF-H_2SO_4 solution) combined with an addition of a known amount of ferrous ammonium sulphate is reliable, as is also the HF-HCl-ICl method of p. 93, if the mineral will dissolve. An advantage of the last-mentioned method is that it will at once disclose whether a rock or mineral is in a state of peroxidation (see p. 94). Such partial information is, unfortunately, of little value to the geologist or mineralogist and in such circumstances the best that can be done by the chemist is to determine total iron, returning it as Fe_2O_3, and to determine total manganese, leaving the geologist or mineralogist to decide in which form it should be returned.

(8) Direct Determination of Soda or Potash

Occasions arise when only one of the alkalis requires to be determined, perhaps on a suite of specimens, and in these circumstances there may be an appreciable saving of time by adopting either of the methods that follow. If both soda and potash are required, there is no advantage to be gained in the matter of time as compared with the standard method described at p. 79. It has, of course, to be borne in mind that these new procedures were devised by E. W. Koenig* specially for alkali determinations on felspars and that, inasmuch as the decomposition in each case is by means of a mixture of hydrofluoric and perchloric acids, the methods are applicable only in those cases where complete decomposition is obtainable by such a mixture. In addition to felspars, these include a number of other ceramic materials such as glasses, china-clays, and china stone. By increasing the amounts of perchloric and hydrofluoric acids used, the usefulness of this method may often be considerably extended.

Provided complete decomposition is obtainable by the acid mixture employed, there is no reason to doubt the accuracy

* "Direct Determination of Sodium Oxide in Feldspar." *J. Am. Ceram. Soc.*, 1939, **22**, 24-31.

"The Semidirect Determination of Potassium Oxide in Feldspars." *J. Am. Ceram. Soc.*, **22**, 164-168.

of these methods, which indeed possess certain inherent advantages. Thus the removal in one operation of the required salt from the bulk of the undesired elements would appear to be preferable to their progressive removal practised in the standard method. Moreover, in the method for soda the use of reagents which might carry sodium as an impurity is eliminated.

The method for soda consists in precipitation as sodium zinc uranyl acetate under carefully controlled conditions. The precipitate contains so little sodium that 1 mg. of sodium will give 0·0669 g. of the triple salt. The amount of sample suggested is for a felspar or other material with a relatively high alkali content.

Reagent. Zinc Uranyl Acetate Solution

Soln. A		*Soln. B*	
$UO_2(CH_3COO)_2\ 2H_2O$	10 g.	$Zn(CH_3COO)_2\ 3H_2O$	30 g.
Water	49 g.	Water	32 g.

The uranyl acetate and the zinc acetate are each brought into solution by gentle warming and stirring. Solution A, however, will remain cloudy owing to hydration of the uranium salt. When solution has been achieved, 6 g. of 30 per cent. acetic acid are added to solution A and 3 g. to solution B. The solutions are then mixed, a few milligrams of sodium chloride are added (to insure saturation with the sodium salt), and a few crystals of barium chloride (to remove any sulphates), and allowed to stand at room temperature for 24 hours.

The clear supernatant liquid is employed as the precipitant.

(a) *Direct Determination of Soda*

0·1000 g. of the finely ground sample is weighed into a small platinum dish, moistened with water, 0·5 c.c. of perchloric acid and 10 c.c. of hydrofluoric acid added, and the mixture evaporated to heavy fuming. It is moistened with water, a few drops of perchloric acid added, and evaporated to practically complete expulsion of acid fumes. After cooling, a few c.c. of water are added, and the dish is warmed on the water-bath until the salts are all in solution, when the solution is transferred to a 30 c.c. beaker. If there is a

slight opalescence, caused by the hydrated aluminium perchlorate, add two drops of perchloric acid. It is convenient to have this beaker marked to show a volume of 5 c.c. and the volume is adjusted, usually by evaporation, to this mark.

The solution is cooled to room temperature (22° C. is considered to be the optimum temperature). 20 c.c. of the zinc uranyl acetate solution which has been brought to equilibrium at the prescribed temperature are added, the solution is stirred to precipitation, and allowed to stand for half an hour at the same temperature.

The contents of the beaker are filtered by suction through a weighed, fritted glass filter-crucible of medium porosity, transferring the residue and washing several times with the reagent. This washing is essential since alcohol will precipitate hydrated aluminium perchlorate from the sample solution, if any be allowed to remain. The final washing is by means of an alcoholic wash liquid (95 per cent. alcohol that has been saturated with sodium zinc uranyl acetate by shaking and digestion). The total volume of washings need not exceed 15 c.c. The filter-crucible and contents are then dried to constant weight in an oven at 80° C. The conversion factor for the triacetate is the remarkably high one of 20·15.

Koenig found the upper precipitation limit under the above-mentioned conditions to lie between 11.8 and 12.6 mg., which on a 0·1 g. sample corresponds to approximately 12 per cent. Na_2O, and which should be just sufficient for theoretically pure albite (11·8 per cent. Na_2O).

Phosphorus, in the amounts found in felspar, causes no interference. Lithium forms a complex with zinc uranyl acetate, so that as in the case of the standard perchlorate method, any lithium present will go with the soda.

(b) *Semi-direct Determination of Potash*

Koenig's investigations have shown that, in spite of the variable composition of sodium-potassium-cobaltinitrite ($K_2NaCo(NO_2)_6 . xH_2O$), sodium-cobalti-nitrite possess the advantage over other specific reagents for potassium in that apparently none of the constituents present in felspar interfere with the complete removal of potassium from a solution

of that material, nor do any of the constituents, other than the alkalis, form compounds with the reagent.

Procedure.—**0·5 g. of finely ground sample is weighed into a small platinum dish, 1 c.c. of perchloric acid and then 15 c.c. of hydrofluoric acid added, and the mixture evaporated on the water-bath to incipient dryness. The dish is then transferred to a hot plate or sand-bath and heated to complete expulsion of fumes. The dry residue is moistened with perchloric acid and again heated to complete expulsion of fumes.**

The residue is moistened with a 5 per cent. calcium nitrate solution* (calcium carbonate, of Lawrence Smith alkali determination grade, dissolved in 50 per cent. nitric acid to give a final 5 per cent. concentration in terms of calcium nitrate) and evaporated to dryness. The residue is dissolved in a minimum of boiling water and transferred to a 30 c.c. Pyrex beaker. If there is a slight opalescence, it may be removed by the addition of not more than 2 drops of nitric acid.

The volume is adjusted to 15 c.c. and the solution is cooled to about 15° C. 1 g. of trisodium cobaltinitrite is added, and the solution is stirred and allowed to stand at this temperature for 15 minutes. It is then filtered through an unweighed Jena B G 4 filter-crucible or its equivalent, the beaker being carefully policed, and the residue is washed once with cold water. The filtrate is discarded.

The remainder of the procedure consists of the conversion of the sodium potassium cobaltinitrite to potassium perchlorate.

The vacuum is carefully released and the receiver changed for one containing a 100 c.c. beaker. The residue is then dissolved directly from the filter-crucible with boiling 50 per cent. hydrochloric acid, the filtrate being received in the beaker by suction. When the solution has passed through completely, the crucible is washed with boiling 5 per cent. hydrochloric acid.

1 c.c. of perchloric acid is added to the solution, which is

* This serves a dual purpose : (1) it decomposes any cryolite type of compound formed, and (2) the free nitric acid converts any alumina formed by heating aluminium perchlorate in platinum to aluminium nitrate.

then evaporated to a point where the salts will just crystallize upon cooling. Evaporation to complete dryness will decompose Co $(ClO_4)_2$ to CoO. If this happens, the latter may be converted to perchlorate by the addition of a few drops of perchloric acid and a repetition of the evaporation. The cooled residue is treated with 15 c.c. of absolute (ethyl) alcohol, the larger particles being broken up with a blunt glass rod and allowed to stand for 10 minutes. The solution is then decanted through a weighed Jena BG4 filter crucible, taking care that no appreciable amount of the residue is brought on to the crucible. The residue in the beaker is treated with 10 c.c. of absolute alcohol, the decantation repeated, and the filtrate discarded.

The residue in the beaker is dissolved in a minimum of hot water, a drop or two of perchloric acid added, and the liquid evaporated to incipient dryness. The beaker is cooled, 10 c.c. of absolute alcohol added, and allowed to stand for 10 minutes. The solution is then filtered through the weighed filter-crucible orginally used, transferring the residue and washing several times with small portions of the alcohol. After sucking dry at the pump, the filter-crucible is heated to constant weight in an oven at 250° C., and weighed as $KClO_4$.

Koenig's results show complete accuracy over the range of 1·9 to 63·9 mg. of K_2O. 1 g. of the reagent is more than enough to precipitate 70 mg. of K_2O completely.

(c) *Other Methods of Alkali Determination*

The conversion of potassium sodium cobaltinitrite to potassium perchlorate, employed by Koenig, was proposed by W. C. A. Guthrie and C. C. Miller (*Mineralog. Mag.*, 1933, **23**, 409-411) and by C. C. Miller and F. Travis (*J. Chem. Soc. Lond.*, 1936, 1390-1394). In the method proposed by these authors, the silicate is decomposed in the usual way by a Lawrence Smith fusion, leached, and the aqueous extract divided; one part is used for determination of sodium as sodium zinc manyl acetate without removal of lime, and part for the determination of potassium by precipitating it as potassium cobaltinitrite and subsequent conversion to perchlorate.

A determination of sodium instead of, or as well as, potassium is certainly desirable when the ratio of potash to soda is very high.

(9) Determination of Ferrous Iron in Refractory Silicates

It is well known that certain of the silicate minerals are incompletely, sometimes very incompletely, attacked by a mixture of hydrofluoric and sulphuric acids, and the determination of their FeO content by the usual Pratt method is in consequence impossible. Silicates noted for their resistance to attack by a boiling mixture of hydrofluoric and sulphuric acids are staurolite, tourmaline, axinite, and the spinels. Even some garnets are prone to incomplete decomposition by this mixture of acids. The foregoing are all rock-forming minerals of fairly common occurrence so that failure, or more usually partial failure, of the Pratt method due to incomplete decomposition is not so rare as might perhaps be thought. It leads of course to a low figure for FeO and a correspondingly high one for Fe_2O_3. The problem becomes particularly serious in the analyses of these minerals themselves, and in such cases all but the recent analyses must be regarded as suspect with regard to FeO. Among lesser-known minerals where the Pratt method fails may be mentioned lusakite (the cobaltiferous staurolite) and kornerupine. Chromite and ilmenite, although not silicates, are iron-rich minerals that are almost unaffected by the usual Pratt method ; they occur in small amounts in many rock types.

Until recently, all the analyst could do was to turn to the Mitscherlich method — decomposition by sulphuric acid in a heated, sealed, glass tube — but as like as not with no improvement in the chemical attack or, as in the author's experience with luskite, with even less success. A pressure tube made of platinum has been suggested. It would certainly allow of the use of hydrofluoric and sulphuric acids at elevated temperature and pressure but would be unduly costly and there would probably be difficulty in completely expelling the air. As Hillebrand points out, the presence of sulphides leads to a high result by this method. In

despair, the analyst has usually had to turn to one or other of the following devices in order to obtain a very rough and probably quite inadequate approximation to the FeO content.

(a) The incompletely attacked residue from the Pratt method is dried, transferred to an agate mortar, ground a little further, and then transferred with a camel hair brush to the platinum crucible for a repeat determination. This procedure is repeated several times until the residue left is negligible.

(b) The undecomposed residue is transferred to a platinum dish, dried, and weighed. The FeO value is then calculated upon the weight of decomposed mineral obtained by difference.

In the author's experience (a) gives rise to low results, and it would appear from the results quoted by H. P. Rowledge* that (b) gives high results. These devices, furthermore, are applicable only to homogeneous minerals and not to rocks containing refractory minerals.

Attempts may be made to carry out prolonged boiling with hydrofluoric and sulphuric acids in an atmosphere of carbon dioxide as described by Mellor† (pp. 512-514). Not only is complete exclusion of air by these methods impossible and the risk of partial oxidation considerable, but the acid mixture may well be boiled away before decomposition is complete.

A further method, suggested to me by Prof. H. F. Harwood, is to fuse the mineral with sodium carbonate in an atmosphere of carbon dioxide, thereafter dissolving the melt in sulphuric acid and titrating with permanganate. Such a method requires the use of a platinum boat and a silica tube, for glass will not withstand the requisite temperature, *i.e.*, the apparatus for determination of total water as shown in Fig. 7 can be adapted for this purpose. By its means a much better result can be attained, but it suffers from one decided drawback in that the sodium carbonate melt effervesces and spatters on the wall of the

* *Journal Royal Soc. W. Australia*, 1934, **20** (for 1933-34) 165-199.

† J. W. Mellor and H. V. Thompson. "A Treatise on Quantitative Inorganic Analysis." 2nd Edn., London, 1938.

tube, thereby tending towards a low result and the swift ruination of the tube, particularly of the transparent section which is so necessary to watch the progress of the fusion. Further, FeO in the presence of platinum can sometimes break down to Fe_2O_3 and Fe, the latter alloying with the platinum (the commonest cause of badly iron-contaminated platinum crucibles); and FeO can reduce CO_2 under some conditions. Moreover, some few minerals would still be incompletely decomposed owing to the temperature being lower than that attainable by direct heating in platinum, *e.g.*, the author found that lusakite required the full heat of a blast Méker burner before it was decomposed by a sodium carbonate fusion.

The method introduced by Rowledge (*op. cit.*) appeared to surmount all these difficulties. Rowledge, after much experimental work on various fluxes, found sodium metafluoborate to be the most suitable. He advocated sealing 0·3-0·5 g. of the sample with five times its weight of flux in a Pyrex tube, supporting the tube in sand in a Morgan crucible while it was heated to 950° C. for fifteen minutes in an electric furnace, cooling and breaking the tube, dissolving the melt in dilute sulphuric acid, and titrating with permanganate.

H. C. G. Vincent* modified this method only to the extent of using silica tubes instead of Pyrex glass, but reported various difficulties. He concluded that "Pending further critical examination of the Rowledge method the figures obtained can be taken as approximate only, for apart from the difficulties of manipulation and trouble due to attack on the tubes, insolubility of the melt, and incomplete attack of the mineral, sources of error are likely to arise from failure to evacuate the tube and also from reduction of ferric compounds during fusion leading to high figures (*cf.* W. Suida, *Min. Mitt.*, **3**, 1876, 175). This aspect of the problem is not discussed by Rowledge but no doubt has accounted partly for the absence of a reliable fusion method for FeO in the past." The author agrees with Vincent only with regard to difficulty in dissolving the cooled melt in dilute sulphuric acid, which is certainly apt

* *Geol. Mag.*, 1937, **35**, 86.

to be troublesome sometimes. Instead of the likelihood of a high result he thinks a low result more probable by reason of (*a*) the air enclosed in the tube, (*b*) the risk of oxidation during the prolonged business of getting the melt into solution by the somewhat primitive method described by Rowledge. An obvious improvement on the Rowledge method is to carry out the solution of the fusion cake by boiling in dilute sulphuric acid in a current of carbon dioxide and subsequent cooling therein before titration with permanganate. Under these conditions, Dr. M. H. Hey, of the British Museum, claims* to have met with no difficulty in applying the Rowledge method. The author has successfully employed a modification of the Rowledge method, which is about to be described.

A few experimental fusions in platinum should be sufficient to convince anyone that sodium metafluoborate is an excellent flux for the rapid and complete decomposition of all the minerals mentioned early in this section. Moreover, it has the great advantage over sodium carbonate that there is no effervescence, the melt remaining tranquil at even the highest temperatures. It seemed to the author that, if the material were fused with sodium metafluoborate in a platinum boat in an atmosphere of carbon dioxide, a silica combustion tube could be used without complications, and this proved to be the case.

Author's Modification of the Rowledge Method

Apparatus.—A translucent Vitreosil tube of $\frac{3}{4}$ inch bore, 30 inches in length, and having a transparent section 4 inches long fused in the centre, is mounted in a gas-heated combustion furnace. In this way, by the momentary removal of a tile from time to time, the progress of a fusion can be watched. Such a tube moreover is the one advocated for the determination of total water (p. 97). If, on the other hand, an electric tube furnace is employed, inspection during heating is not possible. One end of the tube is attached to a supply of carbon dioxide and the other to a bubbler containing phosphoric acid. A convenient size of platinum boat for a $\frac{3}{4}$ inch bore tube is one measuring 7 cm. long by

* *Mineralog. Mag.*, 1941, **26**, 116.

1.27 cm. deep, and 1.6 cm. wide.

Preparation of the Flux.—Rowledge prepared his sodium metafluoborate $(NaF)_2\ B_2O_3$ by heating together a mixture of two parts of anhydrous sodium fluoride and one part of anhydrous boric acid in molecular proportions in a platinum dish at temperatures between 750° and 1,050° C. The operation of preparing and grinding fused boric acid can be omitted with considerable saving of time, and the present author recommends use of the usual orthoboric acid, H_3BO_3, when the components have to be mixed in the proportions 84 of NaF to 124 of H_3BO_3 in order to maintain the required ratio of 84 NaF to 70 B_2O_3. It is best to prepare a quantity of this flux in either platinum or silica. Platinum is preferable as silica is apt to break on contraction of the melt. A gentle heat is applied for a few minutes until the water has been driven off. The full heat of the Teclu burner is then applied and a clear melt results in the course of a few minutes. If the melt is rapidly chilled or is slightly re-heated after cooling, it comes away easily from the container. It is then ground and stored in a stoppered bottle.

Procedure.—0.5 g. of the powdered mineral is weighed into the platinum boat and mixed with six times its weight of the powdered flux. The boat is inserted into the central part of the silica tube, the air is displaced by carbon dioxide, and the furnace allowed to heat to about 950° C., and thus maintained for 15 minutes while a slow stream of carbon dioxide is flowing. The slow current of carbon dioxide is continued until the tube is quite cool. The cold boat is extracted and dropped into 300 c.c. of air-free saturated boric acid solution to which have been added 20 c.c. of concentrated sulphuric acid. A current of carbon dioxide is passed through the flask while the contents are brought to the boil, maintained in that condition until solution is complete, and subsequently cooled under the tap to room temperature and the contents titrated immediately with $N/20$ $KMnO_4$.

If the pink coloration produced by the last drop of permanganate fades within a minute or two it may be taken as an indication that only incomplete solution has been achieved. In this case the solution should be boiled for a

further 10-15 minutes in a current of carbon dioxide, coole(and further permanganate added. Compared with mixture of hydrofluoric and sulphuric acids, tests suggest that th solution is relatively stable and not prone to rapid oxidatio in the air at room temperatures.

More often than not it will be found that the achievemer of complete solution of the fusion is a relatively length business — one hour's boiling is not uncommon. For th reason Hey's method using iodine monochloride in stron hydrochloric acid can be employed (*Mineralog. Mag.*, 194 **26,** 117) with advantage. In this case the platinum boa with the cold solidified melt is placed in a platinum dish an dissolved in iodine monochloride in strong hydrochloric aci (without hydrofluoric acid) in the cold, there being then n necessity to add boric acid, and the iodine released is re oxidized with standard potassium iodate to iodine mono chloride (which thus plays a purely intermediary par serving only to prevent air oxidation of ferrous iron) usin carbon tetrachloride as indicator (see pp. 91-94 for details Hey (*op. cit.*) has also adapted the Rowledge method as micro-method for ferrous iron in refractory silicates.

It would appear that the author's modification of th Rowledge method, coupled with Hey's method of titratio affords nearly a complete solution of what has for lon been the baffling problem of the determination of ferrou iron in refractory silicates. Fusion in a carbon dioxid stream has some risks — a high percentage of FeO migh under some circumstances, reduce carbon dioxide to carbo monoxide — but even these risks would be obviated if stream of nitrogen were used. The behaviour of sulphu in the Rowledge fusion has yet to be ascertained — it migh conceivably reduce a great deal of ferric iron.

A useful tip in connection with removal of the melt fro the platinum boat is to line the boat with a piece of platinu foil.

(10) DETERMINATION OF MINUTE QUANTITIES OF NICKE

A. P. Rollet (*Acad. Sci. Paris Comptes rendus*, 192(**183,** 212-213) devised a very sensitive colorimetric metho for small quantities of nickel, which is based on the fa(

that, after oxidation, an alkaline solution containing nickel dimethylglyoxime turns pink or red in proportion to the quantity of nickel. The simplest procedure is to add about 5 drops of bromine water to a hydrochloric acid solution containing the nickel, then add ammonia until the bromine colour disappears and add 3 or 4 drops in excess, then about 10 drops of a 1 per cent. solution of dimethylglyoxime in alcohol. A series of standard colours should be made up at the same time for comparison. A distinct colour is produced by 0·001 mg. of Ni in 1 c.c. For further details see the following method.

Sandell-Perlich Method

Although the accuracy that can be achieved with small amounts of nickel by this method is comparable with that of spectrographic methods, paradoxically as it may seem, this method is quicker than the gravimetric procedure detailed in Chapter VI, Section 15.

The method described by E. B. Sandell and R. W. Perlich (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 309-311) involves the extraction of nickel dimethylglyoxime by means of chloroform from an ammoniacal citrate solution of the rock sample. By shaking the chloroform extract with dilute hydrochloric acid, the dimethylglyoxime compound is decomposed and the nickel is brought into the aqueous phase, in which it is then determined by Rollet's method. Their procedure is as follows :—

Weigh 0·25 g. of finely powdered basic rock (0·01-0·05 per cent. Ni) or 0·5 g. or more of acidic rock, into a platinum dish, add a few c.c. of water, 0·5 c.c. of 70 per cent. perchloric acid, and 2.5 c.c. of hydrofluoric acid (for a sample greater than 0·25 g. these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0·5 c.c. of perchloric acid and 2 or 3 c.c. of water, and again evaporate to dryness. To the residue add 0·5 to 1 c.c. of concentrated hydrochloric acid and 5 c.c. of water. Heat to bring all soluble material into solution, add 5 c.c. of 10 per cent. sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide, using litmus paper, and add a few drops in excess. If there is

an appreciable amount of precipitate or residue in the solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0·1 gm. of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete a solution as possible. Add 2 or 3 c.c. of 10 per cent. sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material) add 2 c.c. of 1 per cent. alcoholic dimethylgloxime solution, and shake vigorously for one-half minute with two or three portions of reagent-quality chloroform, each having a volume of 2 or 3 c.c. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 10 c.c. of 1 to 50 ammonia solution. Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a c.c. or two of chloroform to recover any suspended drops of chloroform solution.

Shake the chloroform solution of nickel dimethylglyoxime vigorously for one minute, with two portions of 0·5 N HCl, each having a volume of 5 c.c. (or slightly less if the solution is finally to be made up to 10 c.c.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size or a flat-bottomed comparison tube (1·8 by 15 cm.), taking care that no appreciable amount of chloroform is carried over. For colour comparison in a colorimeter the Ni concentration of the final solution should be at least one microgram per c.c. For most acidic rocks the standard series method of colour comparison will usually have to be applied because of low nickel content. A suitable series of standards for a silicic rock is 0, 1, 2 . . . . 10 micrograms of Ni for a 0·5 g. sample. Whether a colorimeter or tubes are used, the final nickel concentration should not exceed 5 micrograms per c.c. or else a precipitate of nickel dimethylglyoxime may be produced.

The unknown nickel solution and the standard solution diluted to about 10 c.c. with 0·5 N HCl are treated simultaneously as follows :—

Add 5 drops of freshly prepared saturated bromine water,

mix, and then add concentrated ammonium hydroxide drop-wise with shaking until the colour of the bromine disappears; finally add an excess of 3 or 4 drops. Next add 0·5 c.c. of 1 per cent. alcoholic dimethylglyoxime solution, mix, and dilute to volume with water if a volumetric flask is used. The colour intensity of the solution increases slowly on standing; the unknown and standard solution should therefore be treated with the reagents at the same time.

If necessary, apply a correction for nickel in the reagents.

Cu, Co, Mn, Cr, and V in the amounts that are likely to be encountered in most igneous rocks do not interfere. Much Cu and Co may lead to high results. Manganese in large quantities may cause trouble by oxidizing nickel to the nickelic condition in the ammoniacal solution during shaking and the results for nickel will then be low, because nickel dimethylglyoxime is not extracted by chloroform.

Under the conditions specified above for the final determination of nickel, Beer's law is closely followed up to a concentration of about 6 micrograms of Ni per c.c. Above this concentration a precipitate may separate.

The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 50 micrograms of Ni per c.c. With a 0·25 g. sample, therefore, the amounts of reagents given above will suffice for percentages of Ni up to about 0·07 per cent.; above this, they must be increased or the method of Harwood and Theobald adopted.

Wells found that the only minerals not easily brought into solution with this method were sillimanite and manganese oxides.*

Sandell (*Colorimetric Determination of Traces of Metals*, *New York*, 1944, pp. 174, 205, 226, 294, 343, and 457) has devised methods, based on the use of dithizone, for the determination of Ni, Co, Cu, Zn, Cd, and Pb on a 2 g. portion of rock powder, but these methods do not appear to be so good for appreciable amounts of Ni or Cu. Large amounts of manganese are also prone to make complete extraction of the heavy metals doubtful.

* R. C. Wells, *U.S. Geol. Surv. Prof. Paper* 205—A, 1943, p. 6.

B. WHEN MATERIAL IS SCANTY

(1) USE OF ONE PORTION FOR $-H_2O$, $+H_2O$, SiO_2, R_2O_3, CaO, MgO, TOTAL IRON, TiO_2, AND MnO.

A 1 g. portion* is weighed out on to a watch glass and hygroscopic moisture determined. As soon as the material has been weighed after drying, it is transferred without loss (mainly by tapping, and finally by means of a camel-hair brush) to the silica boat (previously ignited and weighed) and the combined water determined. The completeness of the transfer is checked by weighing as there may be a loss of a few tenths of a milligram during the operation. The residue from the combined water determination is transferred, without any opportunity for regaining moisture, weighed into a platinum crucible, the silica, R_2O_3, lime, and magnesia determined in the usual way, total iron and titania being determined on the solution obtained by the pyrosulphate fusion of the ignited R_2O_3. If bromine is used with the ammonia precipitation, manganese can be determined colorimetrically on an aliquot part of the solution obtained after the pyrosulphate fusion, but it is more accurate to determine also those portions of the manganese which may have been carried down with the lime and magnesia.

Corrections must be introduced for the loss of both kinds of water and for the material lost in transfer. Nevertheless, with care, a high degree of accuracy can be maintained.

The determination of P_2O_5 on an aliquot part of the solution from the pyrosulphate treatment is not to be recommended as the fusion inevitably leads to loss of phosphorus by volatilization.

(2) USE OF RESIDUE FROM ALKALIS FOR P_2O_3.

The residue from which the alkalis have been leached in the Lawrence-Smith method is rinsed into a small porcelain dish,† dissolved in *nitric acid*, and evaporated to a gelatinous consistency on the water-bath. A certain amount of gentle

* When material is very scanty, this amount may be reduced to 0·8 g., but, unless weighing can be carried out to 0·00001 g., smaller quantities will result in a proportionate loss of accuracy.

† With a platinum dish there is apt to be a slight attack if the residue is dissolved in it.

baking on the sand-bath, coupled with plenty of stirring and breaking down of lumps, is required in order to complete the drying of the silica. The residue is drenched with nitric acid and silica removed. A second recovery of silica is unnecessary. After the careful addition of ammonia (1 : 1) to the filtrate until the precipitate which forms dissolves only on stirring, the solution is ready for the precipitation of phosphorus as ammonium phosphomolybdate and re-precipitation as magnesium ammonium phosphate.

The removal of silica is essential, for otherwise ammonium silicomolybdate will be precipitated along with the ammonium phosphomolybdate, and some of the silica will inevitably be thrown down on re-precipitation of the phosphorus as magnesium ammonium phosphate.

(3) USE OF RESIDUE FROM ALKALIS FOR THE SAME CONSTITUENTS AS IN (1), LESS CaO.

If necessitated by shortage of material, the residue from the alkalis can be used for the determination of SiO_2, R_2O_3, MgO, total iron, TiO_2, but not for lime. In some cases a little of the magnesia may have gone into the main alkali solution so that the magnesia figure is prone to be low by this method. If the water determinations are carried out first, then the alkalis and the other constituents can be determined on the residue, affording a moderately complete analysis on one portion of say 0·8 g.

The residue is dissolved in hydrochloric acid and, after removal of silica, is treated as described in *B* (1) (p. 190), except that after the ammonia precipitation has been made, the bulk of the calcium is precipitated as sulphate by the addition of 2 or 3 c.c. of 50 per cent. sulphuric acid and an equal volume of alcohol. After standing overnight, the calcium sulphate is filtered on a 40 paper, washed with 50 per cent. alcohol, and rejected. The filtrate is evaporated on the water-bath to remove alcohol. The remaining calcium is precipitated in the usual way as oxalate and the precipitate rejected. The filtrate is then evaporated to dryness, ammonium salts destroyed, the magnesia precipitated as quinolate, unless the magnesia content is expected

to be considerable, when the phosphate method will be preferable.

This method is very useful in discriminating between muscovite and talc in very small samples, or indeed in any case where the determination of alkalis is essential and it is desirable to obtain as much other chemical information as possible, no further material being available.

Meier and Stuckert (*Zeit. Anal.*, 1935, **101,** 81) proposed to determine silica, after a Lawrence-Smith fusion, by evaporation with perchloric acid; they did not determine alkalis on this portion. Van Tongeren (*Gravimetric Analysis, Amsterdam,* 1937, p. 76) used the leached residue after a Lawrence-Smith alkali determination for the determination of silica and total iron (by titration).

In the utilization of the leached residue from the alkali determination, it will be found that, if the residue is evaporated directly with perchloric acid, it often gelatinizes and then spurts very badly. The author is indebted to Dr. M. H. Hey for pointing out that it is better to evaporate first with hydrochloric acid, filter off the bulk of the silica and wash, and then to evaporate the filtrates with perchloric acid to recover the rest of the silica. As regards the R_2O_3 precipitate obtained when the alkali residue is utilized, it is difficult to be certain that every trace of the 6·4 g. of calcium carbonate has been eliminated. Instead of igniting the R_2O_3 precipitate, and to obviate this difficulty, Hey prefers to use the R_2O_3 precipitate dissolved in hydrochloric, sulphuric, or perchloric acid for a determination of iron (volumetrically), or to remove ferric chloride by ether and determine titania by cupferron, or, if titanium is absent, to add sulphosalicylic acid, ammonia, and sodium cyanide, boil till a colourless solution is obtained (Fe as Na_4 Fe Cy_6) and precipitate as the 8-hydroxyquinolate.

The foregoing sections provide striking evidence of what can often be done with residues when material is scanty. Indeed, in the analysis of small samples and of minerals in particular, it is an excellent rule not to discard prematurely any solution or residue that is not hopelessly contaminated by additions of reagents.

(4) Determination of FeO, Al_2O_3, Fe_2O_3, TiO_2, CaO, and MgO on One Portion.

Where lack of a micro-balance prevents the adoption of semi-micro methods, the following method is useful for obtaining the maximum amount of chemical information from a small sample of a mineral separated from a rock. When heavy liquid and electromagnetic methods fail to separate a particular mineral constituent of a rock, hand-picking has to be resorted to, and, if the rock has had to be crushed fairly fine in order to avoid composite grains, the separation of only 0·3-0·4 g. may be a very tedious procedure. In such cases, the petrologist or mineralogist is particularly keen to extract the maximum amount of chemical information from the smallest possible sample. These are the conditions for which the following procedure was devised by the author, and by its means the mineralogical position of a pyroxene, amphibole, or garnet in its family group can be decided. Even though the accuracy does not reach the highest standard, the difficulties of the mineral separation and the small amount of material available may justify this procedure. The method is particularly suitable for pyroxenes and garnets where the content of alkalis and water is extremely small, so that a good approximation to the silica value is obtained by difference.

Procedure.—**Not less than 0·3 g. of finely ground material is weighed into a platinum crucible and ferrous iron determined in the usual way, but with *N*/50 instead of *N*/20 permanganate. The contents of the beaker are transferred to a platinum dish, and both the crucible and the beaker are rinsed into the dish. A little extra hydrofluoric acid is added to insure expulsion of all the silica, and the liquid is evaporated to dryness on the sand-bath. 25 c.c. of methyl alcohol saturated in hydrochloric acid are added and the liquid evaporated to dryness again. In this way the boric acid, which was essential to obtain the end-point of the permanganate titration, is removed.**

The residue is then digested with hydrochloric acid, after which it will go into solution on dilution, and R_2O_3 and CaO are precipitated in the usual manner using bromine to bring

down the manganese with the ammonia precipitate. The R_2O_3 can then be corrected for the known amount of manganese added in the form of potassium permanganate. A pyrosulphate fusion is carried out on the ignited R_2O_3 after weighing, and total iron and titania are determined on the resulting solution. The determination of phosphorus on an aliquot part of this solution is not advisable for the reason given on p. 190. Moreover, it is also inadvisable to determine manganese colorimetrically on an aliquot part of this solution, to subtract the amount of manganese added as permanganate, and so obtain by difference the manganese in the original sample.

After precipitation of the lime, 3 g. of nitric acid are added for every gram of ammonium salts calculated to be present, and ammonium salts carefully destroyed. After the removal by evaporation of all the nitric acid, magnesia is most conveniently precipitated by 8-hydroxyquinoline.

Further advantages accrue to the foregoing procedure if the ferrous iron is determined by the alternative HCl-ICl-HF method given on p. 93. In that case no manganese is introduced as permanganate and the addition and subsequent removal of boric acid are also obviated. Manganese contamination can also be avoided with the usual HF-H_2SO_4 solution if the titration is carried out by means of potassium bromate or potassium iodate instead of permanganate, or ceric sulphate may replace permanganate.

Van Tongeren (*Gravimetric Analysis, Amsterdam*, 1937, p. 71) points out that if Pyrex vessels and alkali-free reagents have been used, the filtrate from the magnesium hydroxyquinolate can be further utilized for a determination, of moderate accuracy only, of the alkalis. For this the solution is evaporated with nitric acid and hydrogen peroxide to convert the 8-hydroxyquinoline to nicotinic acid, then ignited with a little sulphuric acid, the alkali sulphates weighed, Na_2O determined in these as sodium uranyl acetate and K_2O obtained by difference. If there is little magnesium to precipitate, it is probably best, as Van Tongeren suggests, to precipitate magnesium with 8-hydroxyquinoline *before* calcium is precipitated with oxalate.

(5) Micro- and Semi-Micro-Methods.

It is not the intention of the author to describe either micro- or semi-micro methods, but, since workers using this book will sooner or later, if they have not already done so, be tempted by considerations of time or forced by the circumstance of shortage of material for analysis to explore or adopt such methods, it may not be out of place to present here some important preliminary considerations with regard to them. In this connection one cannot do better than quote the considered opinion of Prof. H. F. Harwood (*Annual Reports on the Progress of Chemistry. Chemical Society, London.* Vol. for 1937, p. 467) : that "It is quite evident that the micro-chemical analysis of complex minerals and rocks in which a large number of separations are involved cannot yet yield results comparable in accuracy with those obtained by ordinary macro-methods. The present tendency to extol micro-analysis in all cases at the expense of the macro-methods, is, in the Reporter's opinion, entirely unjustifiable. A number of micro-methods, especially those involving organic compounds, such as the micro-Kjeldahl determination, are superior to the corresponding macro-methods, in that they effect a great saving of time and material without any sacrifice of accuracy. In mineral analysis, however, the case is entirely different. Here, a number of determinations have to be made successively on a single weighed portion of material, involving a series of complex separations, whilst the constituents to be determined are usually present in widely differing amounts. Much stress is frequently laid upon the saving of time effected by micro-methods in comparison with macro-ones. In a recent paper dealing with the appliances and methods used for the analysis of minerals on a micro scale (F. Hecht and H. Krafft-Ebing, *Mikrochem.*, 1934, **15,** 39), Hecht rightly gives a warning against the very real danger that any attempt unduly to shorten the time required for a micro-chemical analysis must inevitably result in a loss of accuracy. The saving of time is, moreover, often largely illusory when all the relevant factors are taken into account. Weighings on a

micro-balance consume much more time than those made on an ordinary chemical balance (especially on a modern aperiodic type), and micro-analytical work requires close attention throughout, so that it is not easy to keep a number of analyses in progress simultaneously, as can readily be done on the macro-scale. The carrying out of micro-chemical analyses also demands a highly specialized technique and excellent working conditions, the latter not always readily to be attained. At the present time it is impossible to carry out successfully all types of mineral and rock analyses on a micro-scale since, as Hecht states, the necessary conditions for the separations have in many cases not yet been worked out. Furthermore, when coarse-grained porphyritic rocks are being investigated, composed of minerals differing widely in friability and hardness, and especially when micaceous minerals are present, it seems doubtful if a sample weighing only 30 mg. or so would be truly representative. (See, however, J. Mika (*Z. anal. Chem.*, 1928, **73,** 257) and B. Baule and A. Benedetti-Pichler (*ibid.*, **74,** 442), who deduce mathematically from the theory of probability that a 5 mg. sample should be fully representative. This requires a particle size of 0.001 m.m., and the effects of such fine grinding on the oxidation of the ferrous compounds and sulphides present in the rock cannot be ignored).

"In view of the above facts, it is the Reporter's opinion that micro-analytical methods should be employed for rocks and minerals only in those cases where the small amount of material available renders their use imperative, for otherwise any saving of time and materials effected is more than offset by the diminished accuracy of the results. (F. Hecht, in a private communication to the Reporter, has endorsed the above, stating that in his opinion it is not possible to carry out a complex rock analysis by purely micro-methods with the same degree of accuracy as is attainable on the macro-scale). On the other hand, semi-micro methods do not suffer to such a marked extent from the disadvantages inseparable from pure micro-methods. They can be made to embody the best points of both the micro- and the macro-procedure, and offer a fruitful field

for development in their application to this branch of analysis."

Dr. M. H. Hey, of the British Museum (Natural History), informs the author that his views are similar to those of Prof. Harwood. Regarding micro-methods he writes* : "There is no saving of time and a distinct loss of accuracy (though not so great a loss of accuracy as a few authors would have us believe). My own opinion is that in analyses of moderate complexity the probable error ranges from double to five times that of a macro-determination. In a few favourable cases, this may justify even a second decimal place in percentages, but as a rule I report micro-analyses to 0.1 per cent. only. Difficult separations may be only accurate to 5 or 10 per cent. of the amount there, or even worse if the percentage present is small; but in such separations macro-methods are often not so vastly superior."

"Semi-micro-methods, on one-tenth to one-twentieth the macro-scale (50-100 mg.) on the other hand, usually call for but little modification of macro technique; Lawrence-Smith and Rowledge fusions, paper filtrations, etc., can all be employed, using volumes of solution and amounts of flux, etc., in proper proportion — *e.g.*, where a 250 c.c. beaker is specified, a 25 c.c. one replaces it."

Where the total amount of material available for analysis is around 0·5-1·0 g., Hey prefers to work by normal procedures on a semi-micro-scale rather than by special "scarcity" methods on a macro-scale, especially as the semi-micro-scale usually allows of a repeat or two in case of need.

For semi-micro work a semi-micro balance is, of course, a pre-requisite. If only an ordinary balance weighing to 0.1 mg. is available, the adoption of special "scarcity" methods is obligatory when material is scarce. However, some of the old long-beam balances of the best makers are capable of having their sensitivity increased to somewhere in the region of 60-80 (*i.e.*, 1 mg. displaces the resting point by 6-8 scale divisions) without loss of stability, when they are capable of weighing to approximately 0·02 mg., if due care is taken. The period of oscillation may then be some

* Personal communication.

50-60 seconds, but the additional time spent in weighing is more than compensated by the saving of time on analytical manipulations for a " main portion " can, when necessity demands, be conducted on 0·2-0·25 g. instead of 1·0 g.

For a special study of the application of semi-micro methods to rock analysis, the reader is referred to the paper of Miss W. C. A. Guthrie and Miss C. C. Miller (*Mineralog. Mag.*, 1933, **33**, 405).

CHAPTER VIII

NOTES ON TECHNOLOGICAL APPLICATIONS AND OTHER SPECIAL CASES

On the whole, analyses carried out for commercial and industrial purposes are neither so complete nor attain to quite so high a degree of accuracy as those required for purely scientific work. Nevertheless, in the case of ores, especially, a fair degree of accuracy is required for the objectionable as well as the saleable constituents, and the matter of adequate sampling is no less important than for scientific work. Analyses of rocks and rock-products are being required with increasing frequency for industrial and engineering purposes, and a number of the applications which arise, together with some other special cases, are briefly noted in this chapter.

(*a*) Outline Analyses for Industrial Purposes.

Rock analyses for commercial and industrial purposes should contain most of the thirteen constituents mentioned on p. 28, plus carbon dioxide. Carbon dioxide is of importance as often being more or less proportional to the degree of weathering or decomposition that the rock has undergone. For a like reason the ratio of FeO to Fe_2O_3 is of importance, so that the omission of the ferrous iron determination, which after all saves only half an hour, should not be allowed. The separation of the two alkalis is as essential as the determination of the other major constituents. But for purposes other than scientific, manganese, phosphorus, and titania may often be omitted. Returning the loss on ignition in place of the water content is unsatisfactory in a large proportion of industrial cases. It is more accurate to determine moisture at 110° C. and to estimate the combined water by difference ; no extra time is occupied thereby in

manipulations. The minimum, therefore, is the following nine constituents : SiO_2, Al_2O_3 (plus TiO_2, P_2O_5, and MnO), Fe_2O_3, FeO, MgO, CaO, K_2O, Na_2O, H_2O–110° C., giving a rough approximation to H_2O+110° C. by difference.

Analyses of felspars are among the simplest on account of the very small quantities of iron, titania, manganese, phosphorus, and magnesia which they contain. For industrial purposes, the ammonia precipitate can often be regarded as alumina with a considerable measure of simplification and saving of time in consequence. When silica and alumina or alumina only are required among the constituents usually determined in the main portion, the use of 8-hydroxyquinoline affords rapid routine determinations of alumina from solutions representing 0.1 g. of felspar. Such solutions may be obtained from samples in which silica has been determined, or from individual portions of felspar which have been decomposed by hydrofluoric and sulphuric acids. In the latter case, it is essential that all hydrofluoric acid be expelled from the solution by two evaporations to fuming before attempting precipitation of the alumina. The precipitation is carried out in a slightly acid solution as described on p. 148.

(*b*) Sands, including those for Glass and Refractories.

Glass-sands and sands or rock-products used for the manufacture of silica bricks contain such an extremely high proportion of silica, more often than not exceeding 99 per cent., that modifications have to be introduced in order to determine with accuracy the small amounts of other constituents present. Although ideal sand for the best glass-making is one with 100 per cent. silica (disregarding physical requirements) and such a perfect sand has not been discovered, the ideal is approached by a few sands, including those of Fontainebleau in France (99·7 per cent. SiO_2), Lippe in Germany (99·8 per cent. SiO_2), and Berkeley Springs in the U.S.A. (99·65 per cent, SiO_2). The requirement of a very high silica content, preferably over 98 per cent., and for the best work over 99·5 per cent., is coupled with a low iron content, that for the best glass-work being

below 0·05 per cent. total iron expressed as Fe_2O_3*. Great accuracy is usually required in the determination of iron, the results being sometimes given to three places of decimals. The following analyses of Fontainebleau sand illustrate the conditions encountered in the analysis of a good quality glass-sand (Boswell, *op. cit.*, p. 40).

	Derby Glass Works.	*Barnsley Glass Works.*
SiO_2	99·67	99·80
Al_2O_2	0·19	0·13
Fe_2O_3	0·002	0·006
CaO	0·14	trace
MgO	none	n.d.
Loss on ignition	0·18	0·18
	100·182	100·116

The procedure for such highly siliceous material has to be modified as follows : Silica is determined in the usual way on a 1 g. sample. For the other constituents a 5 g. sample is treated with a mixture of hydrofluoric and sulphuric acids, carefully fumed to dryness, and ignited to expel the last traces of silica. The residue is digested with fairly strong hydrochloric acid and then diluted. R_2O_3 and lime are determined in the usual way, the solutions being kept to a suitably small bulk. Total iron and titania are determined on the solution obtained by pyrosulphate fusion of the ignited and weighed R_2O_3. If the iron is determined volumetrically, it is titrated with $N/50$ permanganate, but a better method is to carry out a colorimetric comparison by any of the standard methods. In every case magnesia will be best precipitated by 8-hydroxyquinoline (see p. 159) in a small volume of liquid after destruction of ammonium salts (see p. 66).

Ferrous iron will be insignificant in good glass-sands, but, if required, it can be determined on a 1 g. sample, using freshly prepared $N/100$ permanganate. Titania occurring principally in ilmenite and rutile, and zirconia in zircon are particularly undesirable constituents for glass manufacture on account of their highly refractory nature.

* P. G. H. Boswell, " Sands and Rocks used in Glass-Making," London, 1918, chap. v.

If the determination of zirconium is required, it may be carried out on a 2-5 g. sample, decomposed first with perchloric and hydrofluoric acids to remove most of the silica, and the residue, even if scarcely visible, ignited and treated with sodium carbonate fusion. However, in view of the fact that the gravimetric method by precipitation of zirconium as phosphate (described on p. 122), usually employed in silicate rock analysis, fails to detect less than 0·01 per cent. ZrO_2, even when using at least 1 g. of sample, a modern colorimetric method may be preferable. The pink lake formed by the zirconium alizarin sulphonate complex has been adapted by D. E. Green (*Analyt. Chem.*, 1938, **20,** 370-372) for the accurate colorimetric determination of zirconia in silicate rocks. The method applies to a range of zirconium oxide content up to 0·275 mg. with an accuracy to 0·003 mg. of zirconium oxide. Hitherto the determination of such small amounts of zirconia in rocks has not been called for, but occasions may arise where the method may prove useful.

A rapid routine method for the determination of silica in glass-sands when only approximate results are required is to heat the sand with fused ammonium fluoride in a platinum crucible and to evaporate the residue with sulphuric acid.* It must be borne in mind, however, that the loss in weight will represent the silica only when no silicates are present. Silicates are also decomposed by the reagent, and the commonest impurity in glass-sand, viz. felspar, will have its alkalis converted to sulphate by the sulphuric acid used. The method is therefore only applicable as a routine check on the silica content of the highest grade of glass-sands. In a rapid method for the analysis of glass-sand, M. B. Vilensky advocates the decomposition of a 1 g. sample with a mixture of nitric and hydrofluoric acids, obtaining the figure for silica by loss of weight after several evaporations to dryness with nitric acid; the other constituents are determined on the filtrate by normal methods.† Unless extreme care is exercised, however, some loss of accuracy with regard to the constituents present in only

* A. C. Shead and G. F. Smith, *J. Am. Chem. Soc.*, 1931, **53,** 483-486.

very small amount seems inevitable. Nevertheless, it has the advantage that one crucible is the only piece of platinum apparatus required.

The analysis of high-grade felspar for ceramic purposes introduces similar problems in the accurate determination of very small amounts of iron. The following references are apposite :—

G. E. F. Lundell & H. B. Knowles. "The Determination of Iron in Glass Sands," *J. Am. Ceram. Soc.*, 1928, **11,** 119-125.

E. W. Koenig. "Analysis of Felspar — Determination of Ferric Oxide : I, Decomposition of Sample," *J. Am. Ceram. Soc.*, 1937, **20,** 230-233.

E. W. Koenig. "Analysis of Felspar — Determination of Ferric Oxide : II, Application of Titanometry," *J. Am. Ceram. Soc.*, 1937, **20,** 233-235.

H. L. Smith & J. H. Cooke. "Determination of Very Small Amounts of Iron," *Analyst*, 1926, **51,** 503-510.

(*c*) Clays and Aluminous Refractories.

The analysis of clays will be carried out by the standard method of Chapter VI. Difficulty may be experienced with the combined water which is sometimes released but slowly. Heating at 1,000° C. for two hours by the direct absorption apparatus will give an accurate result.

The aluminous silicates andalusite, kyanite, sillimanite (Al_2SiO_5), and the artificial product mullite ($Al_6Si_2O_{11}$) are decomposed in the usual way by fusion with sodium carbonate, but the melt should be well blasted.

Refractories consisting mainly of alumina, such as bauxite, are more difficult to decompose by a sodium carbonate fusion. Once the melt is quiet, further heating at about 1,000-1,100° C. for one hour is required. If, however, silica is not to be determined, bauxite can be almost entirely decomposed by a mixture of hydrofluoric, nitric, and sulphuric acids, but burnt refractories are only incompletely attacked by this treatment. For a rapid method for the determination of Al_2O_3, Fe_2O_3, TiO_2, ZrO_2, and P_2O_5 in bauxite and refractories of high alumina content, see Hillebrand-Lundell, p. 868. The determination of alkalis in

high-alumina refractories such as bauxite may require some modification in technique, as described by E. B. Read.*

For a general discussion of the analysis of these materials see "Analysis of Bauxite and of Refractories of High Alumina Content," *Bureau of Standards J. Research*, 1928, **1**, July; also "Chemical Analysis of Clay," by H. R. Shell, *U.S. Bureau of Mines, Rep. Investigations*, 4420, 1949.

The analysis of bricks and other burnt refractories has to proceed on the normal lines of rock analysis as described in Chapter VI.

(*d*) Natural and Artificial Zeolites.

Natural zeolites and the mineral glauconite† have been employed in water-softening plants, but they are now in part supplanted by chemically prepared substitutes. These materials are usually decomposed by strong hydrochloric acid so that a fusion can be avoided. There is nothing difficult about the analysis, all the standard methods being applicable. The mineral glauconite contains 15-20 per cent. or more of Fe_2O_3 as against only a few per cent. of FeO. Potash and combined water are high. Some varieties of glauconite are incompletely decomposed by hydrochloric acid.

(*e*) Pyritiferous Rocks.

If the rock contains only a little pyrite, say less than 1 per cent. of sulphur, a crystal or two of potassium nitrate is mixed with the sodium carbonate before fusion. This oxidizes the sulphur, so preventing the formation of a dark stain of platinum sulphide on the cruible, but there is inevitably a slight attack on the platinum due to the nitre. The presence of nitrate leads to considerably increased effervescence, so the fusion has to be carried out more cautiously than usual, using just sufficient heat to fuse the mixture and no more until the nitrous fumes have disappeared.

When larger amounts of pyrite, or indeed any other sulphide mineral, are present, it is essential to destroy the

* *J. Am. Cer. Soc.*, 1935, **18**, 341-346.

† Mineralogically, glauconite is not classed with the zeolites, though it resembles them in several respects.

sulphide first. With pyrite, chalcopyrite, chalcocite, and bornite this is done by treatment with nitric acid. The material is covered with a mixture of strong nitric and hydrochloric acids in a beaker, placed in a fume-cupboard, and heat from a steam-jet or water-bath gradually applied. The pyrite is decomposed with the evolution of large quantities of brown fumes. When the action dies down, the acid is evaporated to dryness, a little hydrochloric acid added, and this also evaporated to dryness. The residue is taken up with a little hydrochloric acid, the liquid diluted, filtered through a No. 40 paper and well washed. The residue, now freed from sulphur, is ignited, and then fused with sodium carbonate in the usual way. The melt is taken up with hydrochloric acid and the filtrate added after the crucible has been removed. The whole is evaporated for silica in the usual way, *but platinum must not be used for the evaporation.*

The author is indebted to Dr. M. H. Hey for suggesting the following alternative method for destroying excessive quantities of pyrite. Instead of aqua regia, a solution of bromine in 1 : 1 or 2 : 1 hydrochloric acid is used. After decomposition of the sulphides, the liquid is warmed to expel most of the excess of bromine, and filtered. The residue is washed and then fused with sodium carbonate. The filtrates are cleared from remaining bromine with hydrazine hydrochloride ($N_2H_2.HCl$) and added to the soda fusion before evaporation for silica, which, in this case, may be done in platinum. If, however, an excessive amount of ferric chloride is present, attack on the platinum may become a nuisance and the use of porcelain become desirable for this reason.

Certain other sulphides such as pyrrhotite, sphalerite, or zinc blende, are decomposed by hydrochloric acid with evolution of hydrogen sulphide.

(*f*) Coal Ash.

Although the analysis of coal is mainly outside the scope of this book, some notes and references on the subject are perhaps not out of place for the analysis of coal ash presents the usual problems of silicate analysis.

In the proximate analysis of coal, which originated in response to the industrial demand for data on the principal factors affecting its use as a fuel, it is usual to determine only moisture, ash, and volatile matter, and to calculate the fixed carbon by subtracting the sum of these three percentages from 100.

In the ultimate analysis the composition of coal is expressed in percentages of ash, sulphur, carbon, hydrogen, nitrogen, and oxygen, the figure for the last-mentioned being obtained by difference. The sum of the errors involved is thus thrown upon the oxygen. The ultimate analysis as usually made does not distinguish between the carbon and hydrogen of the combustible matter and the small amounts of these elements present in an incombustible form.

In coal analysis it is usual to determine the ash by igniting to constant weight in a muffle furnace at a temperature between 700° and 750° C. Apart from sulphur trioxide, which is almost invariably present, it has been shown that on an average about 95 per cent. of coal ash consists of the four oxides — alumina, silica, lime and ferric oxide.* Magnesia, titanium and alkali compounds are present in small quantities. The chemical composition varies considerably, but usually comes within the limits shown in the following table.†

Typical Limits of Coal-Ash Analyses.

Constituent :	Per cent.
Silica, SiO_2	30—60
Alumina, Al_2O_3	10—40
Ferric Oxide, Fe_2O_3	5—30
Lime, CaO	2—20
Magnesia, MgO	0·5— 4
Titania, TiO_2	0·5— 3
Alkalis, Na_2O+K_2O	1— 4

The principal minerals giving rise to the ash are clay, kaolinite, quartz, felspar, calcite, ankerite, and pyrite. Many others have been reported, but they are usually present in only very small amount. The silica, alumina,

* G. Thiessen, C. G. Ball and P. E. Grotts, *Ind. Eng. Chem., Industrial Edn.*, 1936, **28** (3), 355.

† A. C. Fieldner and W. A. Selvig, " Notes on the Sampling and Analysis of Coal " *U.S. Bureau of Mines, Techical Paper* 586, 1938, p. 22.

titania, and alkalis are mainly derived from the sand, clay and shale, the iron oxide mainly from pyrite, and the lime and magnesia mainly from their corresponding carbonates and sulphates. In coals containing calcium carbonate (as calcite) a large proportion of the sulphur may be retained in the ash as calcium sulphate.

The analysis of coal ash is carried out by the ordinary methods of Chapter VI. For the rarer elements often to be found in coal ash see Chapter XI.

(*g*) Determination of Free Sulphur, Sulphur in Sulphide and in Sulphate, in the Presence of Each Other.

The necessity for some or all of this set of determinations arises in the analysis of rocks containing native sulphur, pyrite, or marcasite, and perhaps alunite, as in certain sulphur-bearing districts of Spain and elsewhere.

Free sulphur is determined first by extracting with an organic solvent in a Soxhlet condenser. The most convenient solvent to use is carbon tetrachloride. After extracting in the Soxhlet condenser for twenty minutes the liquid is evaporated to dryness in a weighed platinum dish on a water-bath. A second and third extraction are then made until the weighings show that all the sulphur has been extracted. Weighed portions of the dried residue from this operation are used for the other two determinations.

Sulphur in the form of sulphide is determined by heating in a current of chlorine and absorbing the sulphuryl chloride in dilute hydrochloric acid. Chlorine from a cylinder, or generated in a flask by dropping concentrated hydrochloric acid on to dry potassium permanganate crystals, is passed through a bubbler containing sulphuric acid, and then through a length of combustion tubing in which the sulphide is contained in a porcelain boat. At the exit end two plain bubblers, or a single train of absorption bulbs, containing dilute hydrochloric acid, absorb the sulphuryl chloride. Corks must be used in place of rubber bungs, and red rubber tubing (of which only a minimum should be used) is boiled in caustic soda solution until it is grey. These precautions

are necessary to prevent the chlorine extracting and carrying over sulphur from the rubber. If much sulphide is present, particularly marcasite, the reaction, which is strongly exothermic, may proceed quite well at first without the application of heat. Heat is applied later and much ferric chloride will be formed. At the close, heating is applied further along the tube, driving as much as possible of the ferric chloride into the absorption tubes. Most of the iron is carried over as ferric chloride. The whole process is completed in about twenty to thirty minutes.

The contents of the absorption tubes are swilled into a beaker. The iron present is precipitated with ammonia in the cold and then brought to the boil and filtered. The sulphur present in the filtrate is precipitated in the usual way with barium chloride, ignited and weighed as barium sulphate (see p. 121).

The total sulphur is determined on another portion of the residue from which free sulphur has been extracted. This is carried out by the fusion method employing either an electrically-heated muffle or an alcohol bunsen burner (see p. 118). The sulphur present as sulphate is then obtained by difference and the figures for the two forms of combined sulphur corrected for the amount of free sulphur which was first extracted.

(*h*) Ultrabasic Rocks and Some Common Rock-Forming Ferromagnesian Silicates.

The analysis of thoroughly basic and ultrabasic rocks is decidedly more difficult than those of the acid and intermediate groups. The first and perhaps the most outstanding difficulty that is encountered is the marked tendency for reduction to metallic iron with consequent alloying of the crucible in the sodium carbonate fusion. This matter and means for getting over the difficulty are dealt with in Chapter IX. Large amounts of either lime or magnesia, or both, are often encountered, so that particular care has to be exercised to insure their accurate separation one from the other. In particular, there must be sufficient ammonium chloride present during both ammonia and lime precipitations to avoid co-precipitation

of magnesia. Likewise, double precipitations are essential.

In the basic rocks chromium or vanadium or both usually become appreciable, as nickel does in the serpentines and olivine-rich rocks. The possible presence of chromite or even native metals of the platinum group must be borne in mind. The difficulty of obtaining complete decomposition by means of hydrofluoric and sulphuric acids increases in the basic rocks, and it becomes necessary to ascertain that decomposition is complete in the ferrous iron determinations.

In the analysis of micas, fine grinding is always extremely difficult and tedious on account of the tendency of the flakes to glide over one another. However, fine grinding is essential, for otherwise decomposition will be incomplete in the Lawrence Smith method for alkalis ; indeed, this is one of the commonest errors in the analysis of micas and a serious one, for their alkali content is always high. The micas, and particularly phlogopite, tend to give off their combined water reluctantly and only at high temperature. The dark micas high in ferrous iron are specially prone to alloying during the main fusion. A retainer for fluorine is necessary for the water determination.

If, in the analysis of biotites or phlogopites, the amount of $KMnO_4$ used in the titration for ferrous iron is found to exceed that required for the oxidation of the whole of the iron present from the ferrous to the ferric state, it should not necessarily be assumed that the titration is in error. J. Jakob has recorded* such a situation in two phlogopites (one from Ontario) and one biotite, and the excess $KMnO_4$ he has allotted in each case to Ti_2O_3 (0·54 - 2·07 per cent.). It will, however, be desirable to repeat both the total iron and the state of oxidation ("FeO") determinations, for such results are certainly abnormal and call for confirmation.

In the analysis of garnets it will sometimes be found that they are incompletely decomposed by hydrofluoric and sulphuric acids in the ferrous iron determination. For treatment in this case see p. 181. In garnets containing an appreciable content of the spessartite molecule the manganese becomes considerable and has to be determined

* Schweiz, *Min. Petr. Mitt*, **1937**, **17**, 149-153.

gravimetrically as on pp. 167-175.

The analysis of pyroxenes and amphiboles usually presents no special difficulties, but a high temperature is required for the expulsion of water.

(*i*) LIMESTONES.

In the past chemists have been very apt to regard limestones, magnesian limestones, and dolomites as pure carbonate materials, whereas these rocks always contain a certain proportion of silica, both in the free state as quartz and combined in various silicates, especially in clay matter, felspars, etc. The situation has been well summed up by W. F. Hillebrand as follows :* "The majority of analyses have been made with reference to their technical utilization and with determination of only the more important constituents. In such cases it has been a common practice to omit direct determination of the carbon dioxide and either to calculate its supposed amount on the basis of the total lime and magnesia found or to regard the loss on ignition as representing the carbon dioxide. The portion insoluble in hydrochloric acid has been frequently stated as silica. Any iron that may have been determined has been reported as Fe_2O_3, water and carbonaceous matter have been overlooked entirely or neglected, as also titanium, phosphorus, and the rarer constituents, and sulphur has been reported almost uniformly as SO_3. Such practice has repeatedly involved very gross errors of omission as well as commission, which, though of little moment in many cases from the commercial point of view, detract much from the value of all these analyses in the eyes of the geologist. . . ."

Limestones frequently contain a certain amount, sometimes very considerable, of the carbonates of iron and manganese. If, then, these constituents are returned as oxides, gross error may result. A careful determination of the carbon dioxide is therefore essential as it is possible to calculate, for instance, how much of the iron in a limestone is present as chalybite ($FeCO_3$) and how much as magnetite, hydrated ferric oxide, or pyrite. Sometimes, however, the case is complicated by the presence of a little gypsum,

* Hillebrand-Lundell, p. 821.

forsterite, diopside, garnet, tremolite, vesuvianite, wollastonite, etc., but such impure limestones are seldom analyzed for commercial purposes. It will be realized, even from this brief statement, that a petrographical examination of a limestone before analysis is highly desirable and likely to be of considerable assistance to the analyst, especially when the limestone is not particularly pure and has suffered metamorphism.

The method of analysis of a limestone is varied quite appreciably according to the proportions of the constituents present. When the insoluble residue is at all appreciable it is filtered off, washed with water (dilute hydrochloric acid if gypsum is present), ignited, fused with sodium carbonate, and treated as an ordinary silicate rock. If petrographic examination shows the insoluble residue to be wholly quartz, or if the residue is too small to warrant separate treatment after the manner of a silicate rock, the silica may be volatilized with hydrofluoric and sulphuric acids. As pointed out by Hillebrand, however, the quartz is much more resistant to these acids than many silicates, so that the treatment may have to be repeated, in some cases several times.

When a complete analysis of the insoluble residue is required in the case of a very pure limestone or dolomite, several grams of the rock are dissolved in acid in order to obtain sufficient insoluble residue to work upon. The whole filtrate may then be used for dissolved iron, aluminium, and manganese, but only an aliquot part of the subsequent filtrate is used for the determination of calcium and magnesium.

When the insoluble residue is not to be analyzed separately, it may in many cases be rendered soluble by igniting to 1,100°-1,200° C. for ten to fifteen minutes ; but this method fails when the proportions are not suited to the formation of a cement. When this is the case, the powdered limestone is heated with not more than 1 g. of sodium carbonate. More than this is not required, as it is unnecessary to attain a complete fusion ; sintering suffices.

The refined analysis of limestones is, however, too long a subject to be treated fully in this volume, and for full

details of methods the reader is referred to Hillebrand or Hillebrand-Lundell.

(*j*) PHOSPHATE ROCKS.

The analysis of phosphate rocks in connection with fertilizers is a routine industrial matter catered for by its own literature, but for those only occasionally called upon to analyse a rock rich in phosphates the following notes may be of some assistance, particularly for those endeavouring to obtain the maximum scientific information as opposed to a routine commercial analysis.

Now that attempts are being made in East Africa and elsewhere to exploit the phosphatic variants of alkaline pipes of the nepheline syenite type for the manufacture of fertilizers, the need for more analyses of silicate rocks rich in phosphates is likely to arise.

The difficulties are such that the running of a continuous scheme of separations, as in the " main portion " of an ordinary silicate analysis is not possible. In nearly all phosphate rocks used as fertilizers the phosphate occurs as fluor-apatite with the result that several per cent. of fluorine may be present. Owing to the difficulty of separating all the fluorine from the insoluble residue left when these rocks are fused with sodium carbonate, no reasonably rapid and accurate method for determining the silica is available. The method outlined below is therefore the best that can be done in the circumstances. Then again the presence of so much P_2O_5 means that the P_2O_5 is usually in excess of all the other members of the R_2O_3 group combined, and when that is the case the usual ammonia precipitate brings down part or all of the alkaline earths and magnesium as phosphates. Iron and alumina, therefore, are determined on separate portions by special methods, though for commercial purposes it is usual to determine only the iron and alumina soluble in (1+1) hydrochloric acid. The difficulty in extracting the fluorine, noted above, leads to the necessity for determining fluorine by a distillation process.

Silica. A 0·5 g. portion is fused with 5 g. of sodium carbonate, leached with hot water, and filtered. The residue is boiled with 50 c.c. of 2 per cent. sodium carbonate for a

few minutes, filtered, and washed thoroughly with hot water, the filtrate being retained. The insoluble residue is ignited in platinum, fused with 3 g. of sodium carbonate, leached with hot water, and filtered. The combined filtrates are retained.

The insoluble residue is transferred to a platinum dish, 1 g. of boric acid powder added (to lessen the effect of the fluorine which is still retained), and then 5 c.c. of nitric acid,* and 10 c.c. of 60 per cent. perchloric acid. The liquid is evaporated until nearly all the perchloric acid is volatilized, cooled, drenched with a few c.c. of concentrated hydrochloric acid and the silica filtered, washed with hot water, and retained. The filtrate is discarded.

The silica in the combined filtrates from the two sodium carbonate fusions is precipitated for the most part with zinc nitrate, and then the remainder with zinc oxide dissolved in ammonium hydroxide, as described under Fluorine, pp. 124-125. The silica obtained in this way is washed into a platinum dish with that obtained from the insoluble residue remaining after the second sodium carbonate fusion. The filter papers used are ignited and the resulting residue added to the platinum dish. The contents of the dish are then evaporated to dryness with 25 c.c. of concentrated hydrochloric acid, the dry residue drenched with strong hydrochloric acid, digested, filtered, and washed with hot very dilute (1+19) hydrochloric acid, and then with hot water. 10 c.c. of sulphuric acid are added to the filtrate, which is then evaporated to fuming. After cooling, the addition of 100 c.c. of water, and short digestion on the water-bath, the small additional amount of silica is filtered off, and washed with hot water. The two filter papers containing silica are then ignited, blasted, and weighed. The silica is then removed by hydrochloric and sulphuric acids in the usual way.

Phosphoric Anhydride. 0·5 g. of the powdered material is boiled with a mixture of 15 c.c. of hydrochloric acid and 3 c.c. of nitric acid for 30 minutes. Ammonium citrate,

* Most of the sedimentary phosphate deposits contain organic matter. In the case of these rocks, therefore, nitric acid should always be used with perchloric acid to prevent the possibility of a serious explosion.

hydrochloric acid, and strong magnesia mixture are then added (*J. Research Nat. Bur. Standards*, 1937, **19**, 59). This together with a second precipitation with strong magnesia mixture in the presence of ammonium citrate serves to separate the phosphate from all the other constituents of a normal sedimentary phosphate rock without the preliminary precipitation with molybdate reagent. This method, however, assumes that the material contains no phosphorus insoluble in this mixture of acids. With finely dispersed apatite enclosed in silicates, as in phosphate-rich alkaline igneous rocks, this condition will not be satisfied. In such cases there will be no short cut from the standard method for phosphorus in silicates given on pp. 107-109, with suitable modification in the quantities of reagents employed and a phospho-molybdate precipitation followed by a double magnesia precipitation being insisted upon.

Total Iron as Ferric Oxide. 2 g. of powdered sample are evaporated in an uncovered flask on a hot plate with a mixture of 30 c.c. of diluted nitric acid (1+2), 5 c.c. of hydrochloric acid, and 10 c.c. of 60 per cent. perchloric acid until fumes of perchloric acid appear. A temperature just below boiling is then maintained until most of the acid has been volatilized. Heating is stopped before dryness is reached. The residue is drenched with strong hydrochloric acid and then digested with 30 c.c. of water on the water-bath until all soluble salts appear to have gone into solution. If the insoluble residue shows any brown or black particles, it is filtered and well washed with hot dilute hydrochloric acid (1+19), and the solution retained. The residue is ignited in platinum, its silica removed by treatment with hydrofluoric and sulphuric acids, and the resulting residue taken into solution in dilute hydrochloric acid (1+19) after a small pyrosulphate fusion. An ammonium hydroxide precipitation brings any platinum out of solution and prevents its subsequent interference in the iron determination. The precipitate is washed once or twice only with water, dissolved in hot dilute hydrochloric acid and the resulting solution added to the main solution obtained above.

Chlorine is first removed from the solution by adding a few drops of a saturated solution of potassium permanganate

and boiling. Stannous chloride solution is then added drop by drop until the iron is reduced, as shown by the disappearance of the yellow colour, any considerable excess of stannous chloride being avoided. The solution is cooled rapidly, 10 c.c. of a saturated solution of mercuric chloride added all at once, the mixture agitated for one minute, and then poured into a 1-litre porcelain casserole (or a beaker with a white porcelain tile below it) containing 20 c.c. of a special manganese sulphate solution and 450 c.c. of water. (This solution is made up by dissolving 200 g. of $MnSO_4.4H_2O$ in a litre of water, a cooled mixture of 400 c.c. of concentrated sulphuric acid and 1,200 c.c. of water added, and lastly 400 c.c. of approximately 85 per cent. phosphoric acid added.) The liquid is titrated with $N/10$ potassium permanganate and a blank carried out on the reagents alone subtracted.

Alumina. It is as well to determine magnesia before alumina, as the method for alumina has to be varied according to whether the magnesia is above or below 0·5 per cent.

2·5 g. of the powdered sample are transferred to a platinum dish, 30 c.c. of diluted nitric acid (1+1) and 10 c.c. of hydrofluoric acid added, and the mixture evaporated to dryness on the water-bath. A further 30 c.c. of nitric acid (1+1) and 5 c.c. of hydrofluoric acid are added, plus 15 c.c. of 60 per cent. perchloric acid, and the contents evaporated nearly to dryness on the hot plate. After cooling, the inside of the dish is washed down with water, another 5 c.c. of perchloric acid added, and the contents again evaporated nearly to dryness. After cooling somewhat, 30 c.c. of diluted hydrochloric acid (1+2) are added, and the contents digested on the water-bath. If there is a residue, it is filtered off, ignited in platinum, and silica removed by the use of one drop of sulphuric acid and about 0·5 c.c. of hydrofluoric acid. After the acids have been evaporated to dryness, the residue is ignited for one minute at 600 to 800° C., fused with a little sodium carbonate, and the cooled melt dissolved in the original acid solution.

The warm solution (60° C.) having a volume of about 200 c.c. is nearly neutralized with a 25 per cent. solution of sodium hydroxide, and is then poured slowly while stirring into 100 c.c. of a 25 per cent. solution of sodium hydroxide

containing 0·5 g. of sodium carbonate. The liquid with its precipitate is transferred to a 500 c.c. measuring flask, cooled, and made up to the mark. The liquid is then filtered through a dry filter into a 200 c.c. measuring flask. A further portion of this solution can be used for the determination of lime.

In this 200 c.c. portion, representing 1 g. of sample, alumina is then determined by the phosphate method as follows :—The solution is acidified with hydrochloric acid and 10 c.c. of the concentrated acid added in excess, and then 1 g. of diammonium phosphate. It is diluted to 350-400 c.c., and, using methyl orange as indicator, is made just alkaline with ammonia, and then the pink colour just restored with a few drops of dilute hydrochloric acid. The solution is then heated to boiling, and 15 c.c. of a 50 per cent. solution of ammonium acetate added. After five minutes boiling the precipitate is collected on a No. 42 Whatman paper and allowed to drain. Then, without washing, the precipitate is returned to the same beaker, the paper stirred to pulp and the precipitation repeated, 10 c.c. of hydrochloric acid and 1 g. of phosphate again being used, the volume being 300 c.c. After filtration, the precipitate is washed free from chloride with a hot 5 per cent. solution of ammonium nitrate.

The paper and precipitate are decarbonized with care, and then ignited at about 1,000° C. to constant weight. Multiplying by 0·418 converts the weight of $AlPO_4$ to the corresponding weight of Al_2O_3. It is recommended that the method should be carried through all the stages, without a sample, in order to obtain a blank, and the result corrected accordingly.

The above method gives low results when 0·5 per cent. or more of magnesia is present. In that case it is necessary to separate most of the magnesium from the aluminium as follows : To the perchloric acid solution of the sample 50 c.c. of hydrochloric acid are added and the volume diluted to 400 c.c. Ammonia is added until methyl orange just turns yellow. The pink colour is just restored by hydrochloric acid, the solution heated nearly to boiling, and 15 c.c. of a 50 per cent. solution of ammonium acetate

added. After boiling for 5 minutes, the liquid is filtered, and the precipitate washed a few times with a 5 per cent. solution of ammonium nitrate. The precipitate is dissolved in 30 c.c. of hot dilute hydrochloric acid and then the neutralization and precipitation with sodium hydroxide commenced.

Lime. A portion of the solution prepared as directed for alumina above can be used for direct precipitation of lime by ammonium oxalate at a pH value of between 3 and 4, *i.e.*, when two drops of brom phenol blue indicator (prepared by dissolving 0·1 g. of the reagent in 1·5 c.c. of 0·1 *N* sodium hydroxide and diluting to 25 c.c.) has changed on the addition of ammonia from yellow to a light green but not to a distinct blue. For a 0·5 g. sample, or 100 c.c. of original acid solution, 50 c.c. of saturated ammonium oxalate solution are added and the volume diluted to 200 c.c. and the temperature raised to 80 to 90° C. before the addition of indicator and ammonia. After two hours on a water-bath, the precipitation is repeated, and the final precipitate ignited, blasted, and weighed as $CaO+Mn_3O_4$. This manganese content is determined colorimetrically by the periodate method and the lime value corrected accordingly.

Magnesia. For the determination of magnesia, lime is first removed by precipitating it as the sulphate in alcoholic solution. Magnesia is then determined in the filtrate (after evaporating the alcohol) by precipitating it as magnesium ammonium phosphate in the presence of ammonium citrate. After re-precipitation it is ignited and weighed as $Mg_2P_2O_7$.

2 g. of sample are boiled in a covered beaker with 15 c.c. of diluted hydrochloric acid (2+1) and 5 c.c. of nitric acid for 10 to 15 minutes. The liquid is diluted with water, digested on the water-bath and then filtered, and the filtrate retained. The residue is ignited in platinum, digested with a little hydrofluoric and sulphuric acids to strong fuming to decompose silicates, diluted and re-evaporated to strong fuming, and finally to dryness, and ignited. The residue is fused with a little sodium pyrosulphate. The cooled melt is dissolved in dilute sulphuric acid and added to the filtrate retained above. 6 c.c. of diluted sulphuric acid (1+1) is

then added to the contents of the uncovered beaker, and evaporated to fuming of the sulphuric acid. After cooling, the inside of the beaker is washed down with a jet of water and the evaporation to fuming repeated. On cooling, 10 c.c. of water are added and the liquid digested on the water-bath with frequent stirring for 10 to 15 minutes. The beaker is removed from the steam bath, 100 c.c. of 95 per cent. alcohol added, the mixture well stirred and allowed to stand for at least half an hour. The calcium sulphate is filtered through a fritted-glass filter-crucible, washed five times with 5 c.c. portions of 95 per cent. alcohol containing 1 c.c. of sulphuric acid per 100 c.c., and the precipitate rejected.

The alcoholic filtrate is evaporated as far as possible on the water-bath. The liquid is transferred to a 300 c.c. flask, diluted to 75-100 c.c., and 2 g. of citric acid and 15 c.c. of a 25 per cent. solution of diammonium phosphate added. Ammonium hydroxide is added until the solution is alkaline to litmus and then 10 c.c. in excess. Some glass beads are added (5—10), the flask stoppered, and shaken on a shaking machine for at least one hour, after which it is allowed to stand in a cool place overnight. After filtration, the precipitate is thoroughly washed with dilute ammonia (1+19), containing 50 g. of diammonium phosphate per litre. The precipitate is then dissolved in hot dilute hydrochloric acid through the paper into the flask in which the precipitation took place, and re-precipitated overnight in a volume of 50-70 c.c., after 0·5 c.c. of 25 per cent. phosphate solution has been added. After filtration, the precipitate is washed with dilute ammonia (1+19). The paper and precipitate are cautiously incinerated in a platinum crucible, and then ignited at about 1,100° C. for 1 - 2 hours and weighed as $Mg_2P_2O_7$. Provided the alcoholic filtrate was clean, the tricalcium phosphate $Ca_3(PO_4)_2$ present will not exceed 0·3 mg. Manganese in the residue is determined colorimetrically, and the weight of $Mn_2P_2O_7$ this represents is subtracted from the original weight of $Mg_2P_2O_7$.

Manganese. This is best determined by the standard method on pp. 104-105.

Fluorine. J. I. Hoffman and G. E. F. Lundell have

shown (*J. Res. Nat. Bureau of Standards*, 1938, **20**, 611) that complete recovery of fluorine by the distillation method of Willard and Winter (*Ind. Eng. Chem. Anal. Ed.*, 1933, **5**, 7) is not achieved unless the fluorine-bearing material is first submitted to a sodium carbonate fusion and then distilled. Without a preliminary sodium carbonate fusion, the result may be one or two tenths of one per cent. low. They recommend a sulphuric acid distillation, thereby avoiding the risks involved in the use of perchloric acid for this purpose when organic matter is present, especially if nitric acid cannot be used as preliminary oxidizer during the heating. They therefore distil from a sulphuric acid solution and determine fluorine in the distillate by the lead chlorofluoride method.

From ·5 to 1·0 g. of powdered sample is fused with 4 g. of sodium carbonate at a red heat for five minutes. Blasting or any higher temperature than necessary for the fusion is avoided. The lower half of the platinum crucible is immersed in cold water to assist in disintegrating the mass, which, when cool, is transferred together with any washings to a 125 c.c. Claissen flask. The round bottom of the Claissen flask sits in a 4 cm. hole in an asbestos gauze or board. The flask has both necks fitted with rubber stoppers, the central vertical one carrying a tap funnel with its stem conveniently bent a little above the rubber stopper to allow a thermometer also to be inserted through the same stopper and to dip in the contents of the flask. The side tube of this special distillation flask is connected to a condenser, the lower end of which is immersed in 20 c.c. of a 20 per cent. solution of sodium hydroxide in a beaker.

About 0·05 to 0·1 g. of 20- to 40-mesh flake graphite or granulated coke is added to prevent bumping, and the flask closed. 30 c.c. of diluted sulphuric acid (1+1) are admitted from the tap funnel, and the flask carefully heated until frothing ceases. The heat is increased until the liquid boils vigorously, and the boiling continued until the temperature of the liquid reaches 160° C. Water is then admitted from the tap funnel at a rate which keeps the temperature of the liquid between 160 and 170° C., 300 c.c. of distillate between these temperature limits being collected.

The alkaline distillate is evaporated to 250 c.c., 3 c.c. of a 10 per cent. solution of sodium chloride added and 2 drops of brom phenol blue indicator (see under lime). Dilute nitric acid is added until the colour changes to yellow and then sodium hydroxide until it is just blue. 2 c.c. of diluted hydrochloric acid (1+1) and 5 g. of solid lead nitrate are added and the mixture heated on the water-bath until the lead nitrate has dissolved. 5 g. of solid sodium acetate are then added, and after vigorous stirring, the liquid is digested on the water-bath for half an hour with occasional stirring. After standing overnight at room temperature, the liquid is filtered through a No. 42 Whatman paper. The precipitate is washed once with cold water, then four to five times with a cold saturated solution of lead chlorofluoride, and then once more with cold water. (The lead chlorofluoride wash solution is prepared as follows : 10 g. of lead nitrate are dissolved in 200 c.c. of water. 1 g. of sodium fluoride is dissolved in another 100 c.c. of water and 2 c.c. of hydrochloric acid added. The two solutions are mixed, the precipitate allowed to settle and the supernatant liquid decanted. Wash four or five times with 200 c.c. of water by decantation. Finally add a litre of cold water to the precipitate and allow to stand for an hour or two with occasional stirring. Filter and use the clear filtrate.)

The precipitate and paper are placed in the beaker in which the precipitation was made, the paper pulped, 100 c.c. of dilute nitric acid (1+19) added, and heated on the water-bath until dissolved. A slight excess of 0·2 N silver nitrate solution (standardized by precipitating a measured portion with hydrochloric acid and weighing the silver chloride) is added, the liquid placed on the steam bath for half an hour, then cooled to room temperature while protected from the light, filtered, washed with cold water, and the silver nitrate in the filtrate determined by means of a standard solution of potassium thiocyanate (0·1 N and standardized by comparing with the standard solution of silver nitrate), using 5 c.c. of cold saturated ferric alum (free from chlorides) to which has been added sufficient colourless nitric acid to bleach the brown colour of the water solution. The difference between the amount of

silver nitrate originally added and that found will be that required to combine with the chlorine in the lead chlorofluoride. One c.c. of 0·2 *N* silver nitrate is equivalent to 0·00380 g. of fluorine.

For short cuts and quicker methods applicable to routine commercial phosphate analyses, reference should be made to the original paper from which the above has been abstracted with a few modifications to adapt the methods more to cases where there is a substantial silicate content. (*Analysis of Phosphate Rock*, J. I. Hoffman and G. E. F. Lundell. RP 1095, or *J. Res. Nat. Bureau of Standards,* 1938, **20,** 607-626.)

(*k*) MINERAL RESIDUES FROM HUMAN SILICOTIC LUNGS — MINERAL DUST — GENERAL SCHEME FOR THE ANALYSIS OF SMALL AMOUNTS OF MATERIAL.

Occasions arise when the determination of twelve or thirteen constituents may be required when very little material is available, perhaps only a gram or so. Such circumstances are frequently encountered in the case of residues from human silicotic lungs, small samples of dust extracted from the atmosphere of underground mines and industrial operations, minerals separated from their associates only with the greatest difficulty, etc.

It may be explained that the residues from silicotic lungs are usually obtained by filtration, washing, and ignition, after destruction of the lung tissue by nitric acid. In consequence, the content of phosphorus is generally higher than in rocks (anything up to 10 per cent.). Ferrous iron in these lung residues is usually so small that it can be omitted without giving rise to appreciable error. Half of one per cent. or more of titania is usually to be found.

The following scheme is suited to all such cases when there is not much less than 1·5 g. available for the analysis.

Scheme.—A main portion of not less than 0·8 g. is taken, and hygroscopic moisture determined first. The residue is used for the determination of combined water, and then for the usual main portion constituents, SiO_2, R_2O_3, CaO, MgO. A pyrosulphate fusion on the R_2O_3 precipitate affords a solution in which total iron and titania are determined.

If bromine has been used in the ammonia precipitation, as on p. 59, manganese may be determined colorimetrically on an aliquot part (say one-fifth) of the initial solution from the pyrosulphate fusion.

Alkalis are determined on a 0·5 g. sample, the residue being used for the determination of phosphorus as described on pp. 190-191.

Ferrous iron is determined on a separate portion of a few tenths of a gram, using $N/50$ permanganate.

(*l*) The Determination of Free and Combined Silica.

With recognition in comparatively recent years of the significance of the silica content of dust, particularly mine dust, in the causation of silicosis, has come the need for discrimination between free silica (present as quartz, chalcedony or opaline silica) and the combined silica (present as silicate minerals). Normally, the determination of free silica can readily be made by petrographic methods,* and there is also an X-ray diffraction method,† but the growing study of industrial dusts in late years has shown that petrographic methods cannot be applied satisfactorily to the fine particles that occur in mine dusts. The demand for determinations of free silica in such dust revealed that no reliable chemical method existed and the matter is still the subject of investigation. Those interested in this subject are referred to the following literature :—

S. R. Rabson. "The Microchemical Determination of Free and Combined Silica in Mine Dust." *J. Chem. Met. & Mining Soc., S. Africa*, 1944, **45**, (3 & 4), pp. 43-57.

A. Salazar and L. Silverman. "A New Method for the Determination of Free Silica in Industrial Dusts." *J. Ind. Hyg. & Tox.*, 1943, **25**, p. 138.

L. J. Trostel and D. J. Wynne. "Determination of Quartz (Free Silica) in Refractory Clays." *J. Amer. Ceram. Soc.*, 1940, **23**, p. 18.

W. R. Line and P. W. Aradine. "The Determination of Quartz in Presence of Silicates." *Ind. Eng. Chem.* (*Anal. Edn.*), 1937, **9**, p. 60.

W. B. Harris. "The Solubility of Quartz in Hydrofluoboric Acid." *J. Ind. Hyg.*, 1937, **19**, p. 464.

* S. H. Shaw. "The Micrometric Estimation of Quartz in Rocks." Trans. Inst. Min. & Met., 1936-7, **46**, 105.

† "Quantative Analysis of X-ray Diffraction. 1. Determination of Quartz." *U.S. Bureau of Mines, R.I.* 3520, 1940.

C. B. Moke. "The Solubility of Quartz in Hydrofluosilicic Acid." *J. Ind. Hyg.*, 1936, **18**, p. 91.

A. Knopf. "The Quantitative Determination of Quartz (Free Silica) in Dusts." *U.S. Public Health Reports*, 1933, **48**, p. 183.

CHAPTER IX

ERRORS

Location of Errors.

Errors may be due to a variety of causes which are conveniently classified as follows :

(*a*) Faulty manipulation and accidents.
(*b*) Use of unreliable methods of separation.
(*c*) Use of impure reagents or faulty balance.
(*d*) Alloying of iron with the crucible.
(*e*) Errors which are only apparent, being arithmetical rather than analytical.
(*f*) Supposed "errors" which are due to the non-determination of certain constituents.

Of these (*b*) and (*c*) should not be allowed to occur and their remedy is obvious. Faulty manipulation and analytical accidents are the cause of the great majority of errors in analyses, though beginners frequently make mistakes in the calculation of their results, due to an incomplete understanding of what they are doing. General carelessness will cause inaccurate results throughout. An error in weighing out the sample for the main portion will affect the silica, alumina, lime, and magnesia, though an error in weighing a precipitate will affect only that particular constituent. Sometimes a careful review of the figures and comparison with average analyses of the rock type in question will indicate the faulty determination, particularly when it is an error in weighing.

Errors are always likely to occur and the most skilled workers are occasionally troubled by them. Thus in the ignition of a precipitate loss may have occurred, unknown to the analyst, owing to an unexpected draught or through mechanical projection. High summations usually indicate incomplete washing of precipitates and incomplete ignition. Low summations are generally caused by losses. If, how-

ever, the operator is convinced that there has been no mechanical loss of liquid or solid, there may have been incomplete precipitation. In this connection magnesia is particularly prone to incomplete precipitation as the double phosphate if the volume of liquid is too large and insufficient ammonia has been added or the mixture has not been allowed to stand long enough.

A common cause of a low result (located in the R_2O_3) is due to reduction of iron to the metallic state during fusion of the main portion; in consequence there is alloying of the iron with the crucible. This may happen whenever silica is less than 50 per cent. and there is high ferrous iron; thus it may occur with any basic rock and especially in the analysis of such minerals as biotite and hypersthene. The effect is in part caused by the reducing atmosphere inside the crucible when it is more or less completely enveloped in a flame, but the reduction is much more marked if a little organic matter is present. In the analysis of ferromagnesian minerals this may well be the case, for they are generally separated from the parent rock in a heavy organic liquid such as bromoform or methylene iodide, followed by washing in benzene or alcohol.

The effect of alloying is usually not noticed until the crucible used for the fusion of the main portion is ignited preparatory to use for another purpose, when a reddish-brown stain of ferric oxide appears on that part of the crucible which has been in contact with the melt. This stain is removed but slowly by hydrochloric acid and the use of fused pyrosulphate is generally necessary. The crucible has, of course, increased in weight, possibly as much as 10-20 mg. If this increase of weight be taken as Fe_2O_3 and added to the weight of the ammonia precipitate, an approximately correct figure for the R_2O_3 can be obtained, but it is necessary, in addition, to remove the iron from the crucible by means of a pyrosulphate fusion. The simplest course is to use this weighed crucible for the determination of the silica and R_2O_3, afterwards carrying out a pyrosulphate fusion on the R_2O_3. Both alumina and iron will then be tolerably correct.

It is clearly advisable to prevent alloying of iron with

the crucible by adding a small crystal of potassium nitrate to the sodium carbonate used in the main fusion. This should most certainly be added if the presence of a little organic matter is suspected, as in residues of dust from human lungs, black shales, and in minerals which have been treated with organic liquids.

Another error that may occur in the analysis of basic rocks arises from the introduction of platinum, which may take place both during the main fusion and during the drying of the residues containing silica. Opinions are divided as to which of the two is the more serious, but there can be no denying that with high iron contents the danger of attack on the platinum dish by ferric chloride during the drying of the silica becomes very real. In extreme cases it may justify the use of a porcelain dish. This platinum is precipitated mainly with the lime, to which it imparts a grey colour after ignition. It is easily removed by igniting the first lime precipitate, re-dissolving, and re-precipitating, for the platinum is thereby rendered insoluble and can be filtered off. Platinum, probably as one of the ammines, may often be seen at the bottom of the dish when the evaporation of the combined filtrates for lime is complete. It is usually of a dirty green shade and should be removed by the method just described.

The most serious errors are those insidious ones which do not show up in the summation ; they are exposed only by careful repetition of the analysis, though they may perhaps be suspected after calculation of the norm. These errors arise from imperfect separation of the constituents. Consider the case of the main portion when there is carelessness or poor technique in effecting the separations. If the silica is insufficiently dried, quite an appreciable amount will escape in solution. Most of this will come down in the ammonia precipitate, but some will also be precipitated with the lime. In bad cases, silica will be precipitated with magnesia and some may even escape in solution. When the content of magnesia is high, as in basic rocks, and if there is insufficient ammonium chloride present, magnesia will be precipitated along with the alumina, and, if the lime is not re-precipitated, appreciable magnesia will be

weighed with the lime. These errors are probably present in most poor analyses and their effect, apart from any others which may be present, will be :

Silica. Low.
Alumina. High by the amount of silica, lime, and magnesia contained.
Lime. High by the amounts of silica and magnesia contained ; perhaps slightly offset by some co-precipitation with the alumina.
Magnesia. Low by the amount of magnesia precipitated with the alumina and lime. This will almost certainly counter-balance any high tendency due to co-precipitation of silica with magnesia.

The analyst who makes the foregoing mistakes, even if he gets his total alkalis correct, will probably fail to separate them accurately. The error in separation soon becomes serious on account of the difference between the factors for conversion of the two alkali chlorides to oxides. It is clear, then, that the nett result will diverge considerably from the truth even though a fair total may be obtained. Unfortunately, others are liable to be deceived, and the only way to put the matter right is to repeat the whole analysis.

In general, when the analysis proves to be faulty, more often than not the error lies somewhere in the treatment of the main portion. The latter is therefore repeated, and perhaps the alkalis as well. If the error is still not apparent, the total water and ferrous iron determinations are repeated. In addition to correcting his errors in this way, the beginner learns a great deal about those points on which he is inclined to err. Indeed, the most satisfactory way of learning rock analysis, or of testing one's skill at it, is to work on rock powder which has been analyzed by an expert, repeating everything until agreement is reached within the accepted limits of error.

Limits of Error.

No analysis can be expected to be perfect nor can it be exactly reproduced on duplication. On account of the complexity of the separations involved this statement is especially applicable to the analysis of silicate rocks and minerals. Nevertheless, good analysts can obtain repeat figures within comparatively small limits of error, which vary according to the proportion of each constituent present. Clearly, more latitude must be allowed for the determination

of silica in a granite (say 70 per cent. SiO_2) than in a similar determination on a melilite-basalt (with perhaps only 35-40 per cent. SiO_2). Moreover, errors may not all be in one direction and may compensate each other to some extent.

As an average for first-class work the author would allow the following limits of error expressed as percentages of the whole rock :

SiO_2	$\pm 0{\cdot}20$	CaO	$\pm 0{\cdot}02$	H_2O	$\pm 0{\cdot}02$
Al_2O_3	$\pm 0{\cdot}10$	MgO	$\pm 0{\cdot}03$	TiO_2	± 0.01
Fe_2O_3	$\pm 0{\cdot}03$	Na_2O	± 0.03	P_2O_5	$\pm 0{\cdot}01$
FeO	$\pm 0{\cdot}02$	K_2O	$\pm 0{\cdot}02$	MnO	$\pm 0{\cdot}01$

The first six figures in this list must be considered decidedly more elastic than the last six. In the analysis of silicate minerals, especially ferromagnesian minerals, certain of the limits can be considerably increased at the expense of others.

Short Totals and Search for other Constituents.

If the total falls short of 100, especially if it is less than 99·75, and the analyst is reasonably sure of the accuracy of his work, it is very likely that one or more constituents which have not been reckoned in the analysis are present in appreciable amount. In this connection it should be remembered that quite a number of constituents are already reckoned in the total even though they may not have been separately determined. Strontia will have been weighed with the lime. Zirconia, beryllia, and rare-earths will have been weighed in the R_2O_3 precipitate. Lithia will have been included in the soda. A number of other constituents such as nickel and copper are partially caught in the principal separations.

Other constituents present, and if not determined, may be responsible for a shortage. Non-determination of carbon dioxide and barium are the most common, and after these come fluorine and sulphur. The determination of fluorine is more accurate and is required more frequently than some authorities suggest.* If the rock contains much mica or amphibole and there is a deficiency, fluorine will almost certainly be the main cause.

* *Cf.* Washington, 1930, pp. 17, 264.

If there still remains a deficiency after all the usual twenty-five or twenty-six constituents have been determined, tests must be applied for boron, carbon, and arsenic, and the mineral composition of the rock must be taken into account, for certain minerals (see pp. 272-274) give up their water at very high temperatures and then only slowly. If any of these minerals are present, the water determination should be repeated using the sodium tungstate fusion method.

If the deficiency still remains, the only practical course to pursue is to have the spectrum photographed on a large instrument, compare it with the photographs for standard R.U.* powder, looking particularly for such constituents as molybdenum, arsenic, zinc, and germanium, which would be missed unless a hydrogen sulphide separation was made. The experienced spectroscopist can be of considerable assistance in such matters. If the spectroscopist cannot find anything then it may be assumed that either the deficiency lies in the water determination or that carbon is present.

ANALYSIS OF LONDON DUST

		Percentage Composition of Ash.
Volatile	51·7	
Ash		
SiO_2	22·2	46·2
Al_2O_3	3·7	7·8
Fe_2O_3+FeO	7·1	11·4
FeO		3·3
MgO	1·2	2·4
CaO	7·9	16·5
Na_2O	1·0	2·1
K_2O	1·0	2·0
TiO_2	0·5	1·0
SO_3	3·7	7·6
P_2O_5	trace	trace
CO_2	trace	trace
Heavy metals	trace	trace
(total	48·3)	
	100·0	100·3

Analyst B. E. DIXON.

* This powder consists of small quantities of fifty elements incorporated in a suitable base, the quantity of each element having been adjusted so that only the "raies ultimes" and the most important sensitive lines appear when the spectrum is excited. On the average about seven lines per element appear.

The analysis, given on p. 229, of London dust* which had lain undisturbed for eighty years is of interest from the point of view of additive errors due to exposure to dust in a city. It shows that rather more than half of such dust is volatile and that silica forms nearly half of the ash derived therefrom.

THE SILICA RESIDUE.

The number of small but complex errors that arise as a result of the residue left in the crucible after the removal of silica with hydrofluoric acid are rather apt to be overlooked, probably because they are small, and are regarded as complex and inevitable. The algebraic sum of these errors, however, is incorporated in the figure for alumina obtained by difference. It is therefore instructive to consider the nature of this residue, as has been done by K. Rankama.†

The amount of residue ranges from a few milligrams in the most acid rocks to about 0·5 per cent. in more basic rocks. In rocks high in titanium and iron the residue may amount to one per cent., and occasionally even more.‡ Hillebrand and Lundell§ state that it may amount to 2 or even 3 per cent. with basic rocks rich in titanium and phosphorus. These two authors, together with Washington, and Dittler|| all agree that the main constituents present in the silica residue from rocks are Al, Fe, Ti and P. Other constituents are Zr, Th, Cb, and Ta, when these are present in the rock. Hillebrand and Lundell state that Ba and Ca are rarely components of the residue, magnesia is only occasionally present, and the presence of alkalis is unlikely. According to Aurousseau** and Beger,†† who have both studied the quantitative composition of the silica residues, titania predominates. The other oxides they found were Al_2O_3, Fe_2O_3, MgO, CaO, and P_2O_5. MnO was not found.

* "Summ. Progress Geol. Survey Gt. Britain for 1934." Part I., p. 84.

† *Bull. Comm. Géologique de Finlande*, 1941, **14**, No. 126, 3-33.

‡ H. S. Washington. "The Chemical Analysis of Rocks," 4th Edn., *New York*, 1930, p. 163.

§ "Applied Inorganic Analysis." *New York*, 1929, p. 726.

|| "Gesteinsanalytisches Praktikum. *Berlin*. 1933. p. 10.

** *J. Washington Acad. Sci.*, 1923, **13**, p. 330.

†† N. Jahrb. 1928. Bd. 57, B.-B., Abt. A., p. 237.

According to these authors it would seem that lime and magnesia are regular constituents of the residue.

K. Rankama (*op. cit.*) applied spectrographic analysis to the silica residues (all obtained under uniform conditions with the use of spectrographically tested reagents) of sixteen analysed igneous rocks with silica contents ranging from 75 down to 41 per cent. He found that as compared with the contents of the elements in the rocks themselves there was a decided tendency to enrichment in germanium, tin, lead, and gallium. A tendency to enrichment existed, though less marked, for zinc, beryllium, nickel, and perhaps chromium. The tendency was towards impoverishment in the case of vanadium, tungsten, and cobalt. Rare earths, aluminium, barium, calcium, iron, potassium, sodium, magnesium, manganese, strontium, titanium, and zirconium were present in all the residues, as was also contamination from the platinum vessels. He concluded that the impurities arose from (*a*) contamination by compounds insoluble *per se*, *e.g.*, titanium phosphate, and calcium sulphate when the washing is insufficient, (*b*) by adsorption of slightly soluble substances produced during hydrolysis, *e.g.*, ferric chloride changing to oxide and oxychloride, (*c*) ionic sorption, which seems to introduce a number of the rarer elements.

In view of the fact that titania is usually the dominant constituent of the residue, particularly when such titania is present in the material under analysis, it is as well in the more basic rocks, and always when there is special reason to expect high titania, to add a few extra drops of sulphuric acid (1+1) before the hydrofluoric acid is added for removal of the silica. If this is not done, there may be some loss of titanium by volatilization as fluoride (Hillebrand and Lundell, New York, 1929, p. 724). There is also a similar risk with high zirconium. On the other hand when much sulphuric acid is added there is the risk of volatilization of some of the phosphorus in the residue on blasting and this loss would then be counted as silica (*op. cit.* p. 556). The reference to " several drops of 50 per cent. sulphuric acid " on p. 55 therefore should be construed as meaning one or two drops in the case of rocks with 60-80 per cent. of silica but with some additional drops as basicity of the rock increases,

making special provision either way when titania or phosphorus are unusually high.

Perusal of this section should have impressed the reader not only with the variety of constituents weighed as R_2O_3 but also of the need, in work of the highest accuracy, of determining singly all those constituents present in the R_2O_3 and of correction for those constituents partially caught with R_2O_3. This need will persist until such time as a suitable direct method of determination of aluminia may become available. The reader will also realize that what is usually referred to as the percentage of R_2O_3 is more correctly described as the percentage of mixed oxides.

OTHER SOURCES OF ERROR.

A cause of discrepancy in an analysis, and one which might possibly be overlooked by analysts who are not also mineralogists, is that some apparently dry, stable minerals and clays, and other rocks containing them, are capable of considerable change in their content of adsorbed or loosely combined water, not only according to the humidity of the atmosphere, but they are also capable of losing much water when stored for some days over a desiccant. Thus certain hydromicas and vermiculites may lose as much as 10 per cent. of water when stored over sulphuric acid and even some geologists might mistake these minerals for highly stable micas.

Another source of error is provided by reaction of reagents with their glass containers, in particular of strong alkalis upon glass. The action of strong caustic soda or caustic potash solution on glass is well known, and for this reason it is usual to prepare the solution from the solid whenever it is required. Caustic alkali solutions are rarely used in silicate analysis, but unfortunately the same cannot be said about ammonium hydroxide. The subject of contaminated ammonium hydroxide is considered by Hillebrand and Lundell (pp. 32-33 and 397). Some interesting data on this point have been published by F. Oates.* Using ammonia solution of 0·880 sp. gr., which had remained for over a year

* *Ann. Rep. for* 1936, *Geological Division, Dept. Lands and Mines, Tanganyika Territory*, p. 12.

in an ordinary glass winchester in the tropical climate of Tanganyika, he found that the addition of the usual quantities (diluted with an equal volume of water) at the several stages required during the course of an analysis produced a distributed error amounting in the aggregate to between 1 and 2 per cent. of the weight of the rock taken. For the conditions in his laboratory, at least, he advocated storage of ammonia not at 0·880 sp. gr. but at half this strength and in wax-lined bottles. Coatings of paraffin wax on glass are, however, unsatisfactory in that they tend to loosen in time, especially in hot weather. If storage of ammonia water in glass for a prolonged period is unavoidable it is probably better to re-distil it at intervals, after first shaking with slaked lime in order to decompose any ammonium carbonate that has arisen from atmospheric contamination.

There is a distinct need for more data both as regards contamination of reagents stored in glass and the effect of reagents on various brands of resistance glass.

Critical Examination of Analyses.

E. S. Larsen in a paper entitled " The accuracy of chemical analyses of amphiboles and other silicates " (*Amer. J. Sci.*, 5th Series, **35,** 1938, 94-103) presents analyses of six amphiboles each of which has been analysed by from two to four " of the better chemists upon whom mineralogists and geologists depend." He deplores the fact that for every amphibole the analysts failed to agree on one or more constituents by as much as 1½ per cent. The lack of agreement was not confined to a few of the oxides but was present in every major constituent, including titania. This lack of agreement was doubtless due in some measure to the fact that up to over two per cent. of fluorine was present and that this fact was not discovered by four of the five analysts concerned. The fifth analyst, the only one named (F. A. Gonyer) is believed to have supplied reliable analyses, and he is stated to have used the methods required for a fluorine mineral. Certainly the divergences cannot all be attributed to the fluorine, and, as Larsen does not comment on them from the point of view of an analyst, it may be of interest to examine some of them here.

Of the six groups of amphibole analyses cited by Larsen we will consider only one, but the student would be well advised to examine the others on the lines about to be indicated.

AMPHIBOLE X.

COMPARISON OF FOUR ANALYSES OF AN AMPHIBOLE.

(Libby, Mont. 16948)

	Analyst A	Analyst B	Analyst D	F. A. Gonyer
SiO_2 .	56·40	56·04	56·28	56·97
TiO_2 . .	·14	tr.	·36	·28
Al_2O_3	·43	1·76	·90	·71
Fe_2O_3 . .	4·14	4·11	4·94	4·71
FeO . .	1·28	1·65	·57	·87
MnO .	tr.	·10	·08	·07
MgO . .	21·82	20·63	22·22	21·95
CaO . . .	8·08	6·56	6·46	6·15
BaO . .	none	none	—	—
SrO . .	—	·02	—	—
Na_2O . .	5·01	5·45	5·04	5·15
K_2O	1·86	2·30	1·74	1·80
H_2O — . . .	·20	·06	·02	—
H_2O + . .	·48	1·02	1·08	·87
NiO . . .	—	·23	—	—
CuO . .	—	tr.	—	—
S .	—	—	.02	—
P_2O_5 . . .	—	·01	—	—
CO_2 . . .	—	none	—	—
Cr_2O_3 . . .	—	·06	—	—
F . . .	—	—	—	1·30
				100·83
Less O for F	—	—	—	·54
	99·84	100·00	99·71	100·29

In the case of amphibole X, the fluorine content of 1·30 per cent. would be expected to cause some but not much loss of silica by volatilization of silicon tetrafluoride during the evaporation with acid. The bulk of the deficiency in silica, especially of analysts B and D, must be attributed either to incomplete drying of the silica or failure to make a second silica recovery. This silica may be expected to be distributed over the alumina, lime, and magnesia, particularly the alumina and lime.

Turning to the alumina figures, that of analyst B is evidently one per cent. high by reason of his failure to prevent co-precipitation of magnesia. This was doubtless caused by the absence of sufficient ammonium chloride,

failure to reprecipitate, or to both causes. That this is so is borne out by the fact that his magnesia is just over one per cent. low. A's low figure seems to be due to incomplete precipitation by ammonia, it is not due to loss, for as might be expected, the deficiency is balanced by an excess in his lime figure. The total irons of the four analysts are from left to right, 5·56, 5·94, 5·57, and 5·67. Three of these are in satisfactory agreement, but unfortunately these three show the most wild variations in their FeO determinations, for which there is no apparent reason. The fact that B gets a high total iron and still gets a very high alumina shows what a lot of co-precipitation of silica, and particularly magnesia, accompanied his ammonia precipitation. B's analysis is so unreliable in other respects that the fact that his FeO is about twice what it ought to be is perhaps less surprising, and still less so when one notes that his summation is 100·00 in spite of the immense mathematical probability against such a happening. Three of the analysts are in satisfactory agreement with regard to manganese; the fact that the fourth records only a trace suggests that he failed to oxidize his manganese to permanganic acid. The fact that B returns only a trace of TiO_2 suggests that he did not make a colorimetric comparison, otherwise it is very difficult to explain.

The fact that A has returned lime 2 per cent. higher than it should be and 1·5 per cent. higher than any of the others is a little difficult to explain. That it is not caused by co-precipitation of magnesia is shown by the fact that his magnesia agrees excellently with that of Gonyer. It appears to be due in the main to precipitation of silica at this point, and more certainly to an incomplete ammonia precipitation. The somewhat high lime returned by both B and D suggests lack of reprecipitation. B's low magnesia is evidently due to co-precipitation of magnesia with the 'mixed oxides.' Three of the analysts achieve fair agreement as regards both total alkalis and their separation, but not so B.

The somewhat high figures for water returned by B and D are evidently due to their lack of use of a retainer for the fluorine. A appears to have employed insufficient heat to drive off all the water (and fluorine).

Larsen stresses the economic factor and concludes that geologists do not usually pay their analysts sufficiently well to expect a first class analysis in return; but the present author would make three further points: (*a*) Three of the analysts, knowing presumably that they were called upon to analyse an amphibole, failed to determine fluorine. This may be because they had not the mineralogical knowledge to know that amphiboles commonly contain fluorine, or they may have taken the commercial attitude that fluorine being a particularly lengthy gravimetric determination should be specially ordered and an additional fee paid. Analysts A and D were satisfied with a short total, which, in the case of an amphibole in particular, was strong suggestive evidence of a substantial fluorine content. Again, the commercial rather than the scientific outlook may have prevailed; but in the case of B it is not impossible that he too originally obtained a short total and decided that it was preferable to recalculate to 100. The need is obvious, therefore, for the closest collaboration between the commissioner of the analysis on the one hand and its executant on the other. All the more is this desirable if, though the executant be a good analytical chemist, he be relatively unversed in mineralogy and petrology. In such cases the geologist should inform the analyst of the mineral or rock type involved and add suggestions as to any constituents over and above the usual thirteen that should be specially sought and, if nesessary, determined. (*b*) Any of these nameless analysts could have checked the accuracy of his analysis by recomputing it on the lines described in Chapter XII. (*c*) It is also worthy of emphasis that duplicate analyses do not necessarily offer any guarantee of accuracy. This is particularly true when the duplicates are carried out by the same analyst. They help to eliminate major errors due to quite a number of causes, but not only do all systematic errors inherent in the methods chosen remain, but many executive errors generally remain, because the two analyses are usually carried on side by side and so partake alike of any over-washing, under-washing, faulty separations, etc. It is desirable instead to make double determinations of at least the principal constituents by methods as different as possible.

CHAPTER X

QUALITATIVE TESTS TO DECIDE WHETHER CERTAIN CONSTITUENTS ARE WORTHY OF DETERMINATION.

In comparatively few cases is it possible to apply a specific test which, in addition to revealing the presence of a trace or more of a certain constituent, gives some idea of the amount present. Carbon dioxide is the one striking exception and the test should always be applied.

Carbon Dioxide.—The test with hydrochloric acid is one of the simplest but it is often carelessly applied. By the adoption of a few points of improved technique the sensitivity of this test is increased very considerably and as little as 0·05 per cent. CO_2 can be detected in a 1 g. sample. The test also serves to show whether any metallic iron has been introduced during crushing.

1-2 g. of the powdered material is placed in a test-tube which is half filled with distilled water. The water is boiled for about three minutes over a bunsen flame, the powder being agitated to prevent it settling at the bottom and perhaps causing the tube to break. The air having been expelled from the powder in this manner, the tube is cooled under the tap, held at about 45° from the vertical and 5 c.c. of concentrated hydrochloric acid added.

With much more than 0·25 per cent. CO_2 there will be an immediate effervescence, but with only 0·1-0·2 per cent. CO_2 or less the tube should be slowly rotated about its long axis causing the powder to be turned over and allow the acid to reach all parts of it. A stream of small bubbles will be observed slowly rising under the upper surface of the tube. If there is no effect or the sample tends to cake, a thin glass rod may be introduced to turn the material over. Amounts of CO_2 from 0·1 per cent. down to a few hundredths of one per cent. may then be detected. With

a little experience the analyst can make a fair guess at the probable carbon dioxide content. If any particles of metallic iron are present, they will give rise to an evolution of hydrogen which has a characteristic odour. Smelling will also disclose the presence of those sulphides which give off sulphuretted hydrogen with acid (pyrrhotite, sphalerite, stibnite, zinkenite, jamesonite, etc.), though the test is rendered more delicate by the introduction into the mouth of the tube of a little paper moistened with lead acetate.

SOLUBLE SULPHATE.—A gram or two of the powdered material is boiled for a few moments in a test-tube with dilute hydrochloric acid (1 : 5), the liquid filtered, and the filtrate tested with barium chloride for sulphate. Haüyne, nosean, gypsum, anhydrite, and some scapolites, but not barytes, will respond to this test. In material containing marcasite, free sulphuric acid may be present. Indeed, in rocks from the neighbourhood of sulphide ores undergoing oxidation sulphates may be plentiful. If, however, hydrogen sulphide has been given off during the test, the formation of a precipitate with barium chloride does not necessarily indicate the presence of sulphuric anhydride in the rock, for it may have been produced by oxidation during the acid attack on the sulphide.

COMBINED TEST FOR BOTH CHLORINE AND SULPHUR, WHETHER SOLUBLE OR INSOLUBLE IN ACID.—2 g. of the powdered sample are fused with sodium carbonate or fusion mixture (in either case free from chlorine and sulphur) in a platinum crucible for twenty minutes over an *alcohol* bunsen burner. A gas flame is useless for this test and an ordinary spirit lamp will not give sufficient heat. The alcohol used must be free from wood spirit, which is likely to contain sulphur; methylated spirit is therefore inadmissable. The cooled melt is leached with hot distilled water (tested free from chloride) over an electrically heated water-bath or the steam jet, *but not over a gas-heated bath*, and filtered. The filtrate is divided into two portions, one of which is acidified with hydrochloric acid and tested with barium chloride for sulphur, and the other is acidified with nitric acid and tested for chlorine (the acids having been tested for their freedom from these constituents). From the degree of

urbidity or the amount of precipitation produced in each ase, some idea of the content of both constituents is btained. Since the operations are not quantitative, they an be carried out comparatively quickly.

Boron.—The best tests for boron are flame tests. In he simplest test of all the powdered material is mixed ith potassium bisulphate and calcium fluoride and introuced on a platinum wire into a bunsen flame. A green ame coloration indicates boron, provided that no other lements are present that might give a green colour (barium, opper, thallium, etc.). This test will not show less than bout 0·2 per cent. B_2O_3 and is therefore useful in rapidly etecting substantial amounts of boron.

For small amounts of boron the following flame test is nost sensitive, 0·1 mg. of boron giving a flame coloration asting six minutes with an air flow of 150 c.c. per minute assing through the test-tube. From 0·1-1·0 g. of powdered naterial is fused with potassium carbonate in a platinum or ickel crucible, and the fusion leached in water. The soluion, or a part of it, is boiled almost to dryness in a testube, and 6 c.c. of methyl alcohol and 1 c.c. of sulphuric cid are added. A stopper is then inserted carrying a glass ube which dips below the level of the liquid in the test-tube nd an exit tube drawn out to a jet. A slow current of air, bout 150 c.c. per minute, is blown through the inlet tube. The mixture of air, alcohol vapour, and methyl borate (if oron is present) passes out of the top of the test-tube, through he jet, through the thin part of a fan-shaped bunsen flame uitably placed for the purpose, and ignites, forming a small uxiliary flame at right angles to the other. The alcohol lame itself is blue-green, but the green imparted to it by oron is quite distinctive and persists so long as an appreciable amount of methyl borate is present. References to a apid method of boron estimation based on the persistence f this flame coloration are given on p. 147.

Arsenic.—It may be worth while testing for traces of this onstituent when the specimen is of a rock containing sulhide minerals or is from a mineralized district.

A most sensitive and reliable test for arsenic has been levised by Gutzeit. A small flat-bottomed flask, such as

those used in carbon dioxide determinations, is fitted with a rubber stopper through which passes a short glass tube sealed at its lower end but having a small hole blown on one side. Lumps of a sodium carbonate melt of the material under test are placed in the flask together with pure zinc (free from arsenic). A roll of filter paper soaked in lead acetate is inserted into the tube. Dilute hydrochloric acid is added to the contents of the flask, and a filter paper moistened with mercuric chloride solution is placed on top of the tube. Arsenic, if present, will be converted to arsine, AsH_3, which in escaping up the tube gives rise to a yellow to black stain on the mercuric chloride paper, the depth of the stain being a rough measure of the amount of arsenic present. The lead acetate paper is required to free the escaping gases from traces of hydrogen sulphide.

FLUORINE.—In the first edition of this book it was stated that a simple test to ascertain whether appreciable fluorine is present in a rock or silicate mineral would be very welcome, but that none of those put forward up to that time could be relied upon. The author has since investigated the test published by Feigl.* That test is indeed extremely sensitive, so much so in fact that the greatest care has to be taken to avoid contaminated glassware or reagents. Feigl points out that rocks containing carbonate or sulphide require preliminary calcination before testing and would appear to suggest that, apart from this, the test is applicable to all silicate rocks. This, unfortunately, is not the case. The test depends on the evolution of silicon tetrafluoride on heating with strong sulphuric acid. It will reveal fluorine, therefore, only when a fluorine-bearing mineral decomposable by sulphuric acid is present. Thus it will readily reveal the fluorine in fluorspar or fluor-apatite present in a silicate rock, but it fails to release the fluorine in pyroxenes, amphiboles, or tourmaline, and topaz is only partially attacked by sulphuric acid. It works well with biotite, phlogopite and lepidolite, either on mineral specimens or on rocks containing them. Thus it gave a good reaction on a centigram of granite, 9 per cent. of which consisted

* "Qualitative Analysis by Spot Tests," 3rd Edn., English Translation, 1947.

of biotite containing 0·22 per cent. fluorine. Since of the other minerals present, the hypersthene would not be attacked by the acid, and the quartz and felspar would not be expected to contain an appreciable amount of fluorine, it is probable that in this instance the test revealed the presence of not much more than 0·02 per cent. fluorine. On the other hand, it failed on a muscovite powder containing 0·11 per cent. fluorine. Thus the test may reveal a minute quantity of fluorine in a small amount of apatite present in a rock, yet fail to disclose the much larger amount present in an amphibole or a mica resistant to sulphuric acid. Hence the author advocates the use of the test only when no silicates are present that usually contain some fluorine. If they are present, then fluorine should in any case be determined gravimetrically or by Steiger's method. If the mineralogical constitution of the rock is unknown, then no reliance can be placed on the test except when a positive reaction is obtained. The test is most useful in showing whether a biotite contains only a little fluorine suitable for estimation by Steiger's method or a greater quantity demanding the gravimetric method. Taking samples of 50 milligrams for test, a blue coloration with a slight blue precipitate usually indicates the suitability of the Steiger method, while a dense, flocculant, blue precipitate suggests the need for the gravimetric method.

The test depends on generation of the volatile silicon tetrafluoride, which, when absorbed in a drop of water, produces silica and fluosilicic acids. These are then converted with ammonium molydbate into silicomolybdic acid. The latter can be identified, since, unlike free molybdic acid, it oxidizes benzidine in acetic acid solution to a blue dyestuff, with concurrent production of molybdenum blue.

A small test-tube, three or four inches long and of rather narrow bore, is fitted with a cork through which passes a fairly stout glass rod with a rounded lower end arranged so that it reaches to about $\frac{3}{4}$ - 1 inch from the bottom. 50 - 100 milligrams of finely powdered rock or mineral are placed in the bottom of the tube and 6 to 10 drops of strong sulphuric acid added. The rod is then wetted for its whole length and carefully inserted so that a drop of water hangs

from its lower end. The acid is carefully heated over a small flame so that it boils very gently for one minute. The tube with its rod and drop are then stood in the test-tube rack for 5 minutes. The cork and rod are carefully extracted, and the liquid on the rod swilled with six to ten drops of water from a wash-bottle into a white porcelain crucible. Two drops of ammonium molybdate solution are added (15 g. of ammonium molybdate dissolved in 300 c.c. of water and poured into 100 c.c. of nitric acid) and the crucible heated gently until its contents begin to bubble, after which it is allowed to cool. When quite cool, one drop of a one per cent. benzidine solution in 10 per cent. acetic acid is added. Then, on the addition of several drops of a saturated solution of sodium acetate, a blue colour and blue precipitate are formed if fluorine is present.

It is advisable first to carry out a blank with the reagents alone to ascertain that the fluorine is actually in the material under test.

The following modification of the zirconium-alizarin colorimetric determination of fluorine in water which has been described by F. C. Foley and P. W. West (*Amer. Min.*, 1939, **24**, 398-399), affords a useful qualitative test especially for fluorine in minerals. It depends on the fading of a zirconium-alizarin lake in the presence of fluorine, the pink colour fading to yellow, the degree and rate of fading being directly proportional to the amount of fluorine present.

The zirconium-alizarin indicator is prepared by dissolving (*a*) 0·17 gm. of alizarin sodium sulphate in 100 c.c. of water, (*b*) 0·87 gm. of zirconium nitrate in 100 c.c. of water, and adding (*a*) to (*b*) slowly and with constant stirring. The sensitivity of this indicator persists for about six months, if it is kept in a cool, dark place.

A sodium carbonate bead is prepared on a platinum wire and a little of the powdered mineral is fused into it. The bead is then dissolved in 1 c.c. of 1+1 hydrochloric acid in a test tube, and then diluted to 5 c.c. with water. Two drops of indicator are added and mixed. Fading of the original pink colour indicates presence of fluorine. If the fading is at all in doubt, it is advisable to prepare a blank

of 1 c.c. of 1+1 hydrochloric acid diluted to 5 c.c., with two drops of indicator added. Fading is then usually noticeable in two to three minutes, though very small quantities may require as long as twenty minutes. With slight fading it is advisable to use a white background.

Large amounts of phosphates, sulphates, arsenates or sulphides cause some fading of the lake. In such cases a Willard-Winter distillation is required and the test carried out on the distillate, but this will seldom be required with silicate rocks and minerals.

CHROMIUM.—A red alcoholic solution of diphenylcarbazide has been shown by G. H. Leitmeier and F. Feigl* to turn violet in the presence of only a trace of chromate. The material to be tested is first fused with sodium carbonate on platinum foil or a crucible lid, when any chromium will be converted to sodium chromate.

MANGANESE.—Manganese will almost invariably be present in rocks in amount worthy of determination, so that the test, excellent though it is, need rarely be applied. In certain silicate minerals — *e.g.*, garnets with a considerable content of the spessartite molecule — the manganese content is too great to allow of the colorimetric method and has to be determined gravimetrically. If the amount of material is limited, it may be very useful to ascertain the order of magnitude of the manganese content on a small portion, say 1 or 2 cg., before the actual analysis is commenced. The test is best carried out as follows :

0·1-0·2 g. of finely powdered material is placed in a small crucible and about 3 c.c. of a mixture of equal parts of 50 per cent. sulphuric acid and hydrofluoric acid added. The mixture is evaporated to strong fuming on the sand-bath, cooled, water added, and re-evaporated to strong fuming. With such small quantities the evaporations do not take more than twenty minutes each. Water is added, bringing the volume up to 20 c.c., and then, without filtration, about 5 mg. of potassium periodate are added. The mixture is gradually brought to boiling point and allowed to cool, when the depth of colour will be proportional to the manganese present, and a very rough colorimetric comparison

* *Min. Petr. Mitt.* (Tsch.), 1931, **41**, 95-102.

may be made using $N/50$ or $N/100$ $KMnO_4$.

COPPER.—If copper is present in a form other than silicate, it may be extracted with acid and easily tested.

Most Sensitive Method.—2 g. of material are boiled with strong nitric acid for ten minutes. An equal volume of water is added and the liquid filtered. If a sintered glass filter crucible is used, dilution is not necessary. The filtrate is evaporated to dryness in a porcelain dish to remove the nitric acid. The residue is dissolved in 1 : 1 hydrochloric acid on the water-bath. When solution is complete, the liquid is made up to 200 c.c., brought to the boil, and an ammonia precipitation carried out using several c.c. of dilute ammonia in excess. The liquid is filtered through a double 41 filter paper, 50 c.c. portions of the filtrate being used for testing. When 5 c.c. of a 0·1 per cent. aqueous solution of sodium-diethyl-dithiocarbamate are added, a yellow colour is produced if copper is present even in minute traces. A brown coloration indicates incomplete precipitation of iron, in which case add more ammonia to one of the unused portions of the filtrate, boil, and filter through a double filter paper before repeating the test.

The above test is sensitive in the extreme, and, if appreciable copper is present, the colour will be deep or more probably pass into a turbidity. If turbidity is developed, dilute another portion and test again. The test which follows is much less sensitive, its lower limits being somewhere in the neighbourhood of the upper limits of the previous test — *viz.*, 0·1 per cent. CuO on a 2 g. sample. The limits of the first method are brought above this figure only by dilution.

Less Sensitive Method.—The powdered material (about 2 g.) is boiled with nitric acid as before, filtered, and an ammonia precipitation carried out with several c.c. of dilute ammonia in excess. On filtration the filtrate will show a tinge of blue if several tenths of one per cent. of CuO are present. If no colour is visible or it is so faint as to be doubtful, the filtrate is transferred to a large white porcelain dish and evaporated to small bulk on the water-bath, a few drops of strong ammonia being added to keep the liquid ammoniacal. Even though this test fails to indicate copper there may

nevertheless be sufficient to afford significant data to the petrologist.

Molybdenum.—It is sometimes desirable to test for molybdenum in acid granites, where it may occur as molybdenite, MoS_2. This mineral, fortunately, is soluble in strong nitric acid. The powdered material is therefore heated in a porcelain dish with several c.c. of concentrated nitric acid. After dilution with double the volume of water, the liquid is filtered, sulphuric acid is added to the filtrate which is evaporated to small volume on the water-bath, and then evaporated in a porcelain dish over a small flame. As the last of the acid is being removed a beautiful deep blue is developed if molybdenum is present. This test is a very sensitive one, but, inasmuch as it depends on the reducing action of charred dust, filter paper fibre, or other organic matter, it can occasionally fail even though molybdenum is present. For this reason the xanthate test described below is recommended as being more certain and more characteristic.

For rocks or minerals use a 1 g. powdered sample, add 15 c.c. of nitric acid, 10 c.c. of hydrochloric acid, and 5 c.c. of sulphuric acid, boil to dense fumes of sulphur trioxide if molybdenite or other acid-soluble molybdenum mineral is anticipated. Hitherto most testing for molybdenum has been confined to these acid-soluble minerals, but the simplicity and sensitivity of the xanthate test should encourage search for molybdenum in the silicates, and for this purpose it will be necessary to open up with a mixture of sulphuric and hydrofluoric acid in the usual way, finally bringing the sulphuric acid to strong fuming. For testing a sulphide precipitate, it can be ignited in porcelain, and digested and fumed with sulphuric acid. For solutions, add 5 c.c. of sulphuric acid to 25 c.c. and boil to strong fuming.

The fuming acid digest obtained as above is cooled, about 20 c.c. of water added, and boiled until all soluble salts are in solution. Strong caustic soda solution is then added until slightly alkaline, the liquid boiled for a few minutes, and allowed to settle. The volume should not be over 100 c.c. at this stage. 10 to 20 c.c. of the liquid is decanted through a filter paper into a test-tube and about 0·1 g.

of solid potassium ethyl xanthate added, followed by one or two drops of concentrated sulphuric acid. The presence of molybdenum is then indicated by a light pink to deep purple colour, depending on the amount of molybdenum present.

The solution should be filtered, even if it appears clear, for otherwise small amounts of copper and iron precipitates may produce a brown or yellow precipitate with the xanthate before the final addition of sulphuric acid. Any alkaline xanthate may be used for the test, but potassium ethyl xanthate is preferable. Using a 1 g. sample and making the solution up to 100 c.c., 0·0025 per cent. Mo is detectable, and 0·005 per cent. with ease.

Other metals which give coloured compounds with xanthates are nickel, cobalt, and chromium, but these, like iron and copper, are removed by the caustic soda precipitation. Vanadium also gives a colour, but does not interfere except where the ratio of vanadium to molybdenum is extremely high. In such an unusual case the two elements can be separated by precipitating the molybdenum with sulphuretted hydrogen in acid solution and testing the precipitate; but a better procedure in that case is to employ the thiocyanate-stannous chloride-ether test for molybdenum, as employed by Sandell, when vanadium will not interfere.

It should be pointed out that Sandell's colorimetric method for molybdenum (which can be done on the same portion as chromium and vanadium) does not take much longer to carry out than the xanthate test described above (*Colorimetric Determination of Traces of Metals*, New York, 1944, pp. 335-336).

VANADIUM.—A simple test for vanadium* depends on the fact that this element will colour a cooled potassium pyrosulphate melt yellow. The intensity of the colour was found to be more than twenty times as great as that of the colour given by any other element. For use as an approximate method for determining amounts of V_2O_3 up to about one per cent., the method has to be carried out under standard conditions as described by Axelrod, but the test may be

* J. M. Axelrod. *U.S. Geological Survey Bulletin* 950, 1946, pp. 19-23.

applied to most rocks to ascertain whether more than a few hundredths of one per cent. of V_2O_3 — that is whether more than the usual amount of vanadium — is present.

The powdered rock is heated with a coarsely powdered flux (consisting of five parts of potassium pyrosulphate to one part of potassium nitrate) from 1 to 2 minutes to a bright red heat (about 750° C.) in a small Pyrex test-tube. Iron colours the molten or hot melt yellow to brown, but on cooling this colour disappears and in most cases a yellow colour will denote vanadium. Uranium, nickel, and cerium also give a yellow colour, and several other elements interfere to a lesser extent by giving rise to other colours. A 0·01 c.c. sample containing 0·25 per cent. of V_2O_3 yields a melt about the colour of solid potassium chromate, in the absence of interference, and 0·02 per cent. is said to be detectable.

If Sandell's method for chromium and vanadium is employed (*Colorimetric Determination of Traces of Metals*, New York, 1944, pp. 195-445), it has the great advantage that the brown of V-8-hydroxyquinoline in chloroform is very characteristic and specific; it even gives a rough qualitative idea of the vanadium content long before the determination is completed. Indeed the older chromium-vanadium technique of pp. 129-132 may be replaced by Sandell's method for Cr, V, and Mo with confidence.

Beryllium.—The following,* unlike most spot tests, is not highly sensitive and will not detect much less than 0·8 per cent. BeO. It is, nevertheless, of considerable value in demonstrating that beryllium is present in quantity demanding its special separation. It can also be used for confirming the identity of the BeO obtained by the method on pp. 148-149. The method involves the use of p-nitrobenzene-azo-orcinol as a spot test reagent.†

About 1·5 g. of caustic soda (conveniently reckoned by the number of pellets required) is melted in a nickel crucible, heated to a dark cherry red, and allowed to cool. About 0·1 g. of the powdered material under test is added to the

* F. Kulcsar. *Eng. Min. J.*, 1943, **144**, 103.

† A. S. Komarowsky and N. S. Polucktoff. *Mikrochemie*, 1933-4, **14**, 315. F. Feigl. "Spot Tests." 2nd English Edn., p. 121.

crucible, and the melt is again heated to a cherry red, this time for five minutes. The melt is allowed to cool completely and stood in a large dish of cold water, the level of the water coming about half-way up the outside of the crucible. 10 c.c. of cold water are added to the crucible and the contents stirred until the melt has completely dissolved, the crucible being kept cooled by the water throughout the process of solution.

With a stirring rod, two drops of p-nitrobenzene-azo-orcinol solution are placed on a double thickness of filter paper, and on this same spot is placed a drop of 25 per cent. potassium cyanide solution. In the centre of this large spot, a small drop of the solution from the nickel crucible is then placed. A pink coloration of the spot will indicate the presence of beryllia.

The p-nitrobenzene-azo-orcinol solution is prepared by dissolving 0·025 g. of the reagent in 100 c.c. of normal (4 per cent.) caustic soda solution. Warming the beaker slightly aids in dissolving the reagent. Any turbidity that develops should be allowed to settle and only the clear solution used. The solution should be kept in a rubber-stoppered bottle, and should not be used until the reagent is completely dissolved or misleading red flecks will be produced in the test. Since the reagent solution keeps for only two weeks, and in most laboratories it is not likely to be required frequently, it will generally be better to make up a small quantity of the fresh solution whenever required.

The best light for the test is bright daylight, but not direct sunlight. If the beryllia content is small, the colour may appear only slowly, but if no colour has developed by the time the spot is dry the beryllia content is less than 0·8 per cent. The colour fades on drying. It is as well to have a mineral powder or *freshly prepared* solution containing approximately 1 per cent. BeO as a control.

A more sensitive test for beryllium has recently been described by M. H. Fletcher and C. E. White (*Amer. Min.*, 1946, **31**, 82-83). A bead of fusion mixture is made on a loop of platinum wire, and to it is added a particle (about 40 mesh) of the mineral to be tested or an equivalent amount of powdered material. The bead is heated again to decom-

pose the sample, and then dissolved in 6-8 drops of 1+1 hydrochloric acid in a small test-tube. The solution is cooled and 2 drops added of either of two dyes (1-4 dihydroxyanthraquinone (quinizarin) or 1-amino-4-hydroxyanthraquinone, both at 0·03 per cent. concentration in chemically pure acetone). Avoiding exposure to sunlight, sodium hydroxide is added dropwise until the solution is purple; an excess must be avoided. The solution is then exposed to a long-wave ultra-violet lamp in a darkened room. If beryllium is present, a strong orange-red fluorescence appears. The solution may be tested in the original test-tube, but it is better transferred to a non-fluorescent porcelain spot plate.

If iron or manganese hydroxide precipitates upon addition of the sodium hydroxide, the test is modified as follows: 1-2 mg. of the powdered material is boiled with 6-8 drops of 1+1 hydrochloric acid in a small test-tube. After making alkaline with an excess of sodium hydroxide, the solution is filtered into a clean test-tube, cooled, and two drops of the dye solution added. Hydrochloric acid is added dropwise until the purple colour disappears and then sodium hydroxide until the solution is again purple. It is then examined for fluorescence.

Lithium gives the same reaction, but, if the small samples recommended are used, a negative test is obtained even with lithium-bearing minerals.

For a photometric method of determination of beryllium in its minerals and in rocks containing them see G. H. Osborn and W. Stross, *Metallurgia*, 1944, **30**, No. 175 (May), p. 3-6.

Uranium.—In view of the great importance attained by uranium and the official inducements now being offered for its location, the desirability of testing for its presence in rocks and minerals is correspondingly enhanced. The Geiger counter affords the most sensitive test; other physical instruments are much less sensitive, *e.g.*, the simple electroscopes and the spinthariscope are suitable only for high grade uranium ores. In the absence of a Geiger counter, the following chemical tests will be found useful in detecting relatively small amounts of uranium.

(*a*) Unfortunately there is as yet no really specific spot

test for uranium, for, although the potassium ferrocyanide test in the absence of interfering elements is extremely delicate, it is affected by ferric and cupric salts and titanium, all of which give coloured ferro-cyanides. This is especially unfortunate inasmuch as these elements are particularly prone to be present. In the following modification of the tests the effects of the first two salts are overcome.

A pin-head sample of a mineral, or more in the case of a rock, is finely ground and fused with sodium carbonate on a loop of platinum wire. On cooling, the bead is evaporated to dryness with hydrochloric acid on the lid of a platinum crucible. The residue is then moistened with a drop of acid and diluted with a little water. A drop of this acid liquid is placed on a spot plate, and one drop of 10 per cent. sodium thiosulphate solution added which will reduce any ferric and cupric ions present. The addition of a drop of 3 per cent. potassium ferrocyanide solution should produce a brown colour or precipitate. Titania, if present, gives a yellow stain, which gradually turns brown. Distinction can be achieved by mixing the test solution with ammonia, warming gently, and acidifying with acetic acid. Under these conditions uranyl hydroxide goes into solution while titanium hydroxide does not. Filter and carry out the potassium ferrocyanide test on the filtrate.

(*b*) The following bead test, if a few simple precautions are observed, is extremely delicate, and, under favourable conditions, allows of the detection of 0·01-0·05 microgram of uranium. It requires the use of a long-wave ultra-violet lamp,* and a good grade of sodium fluoride. The latter should be tested by making a bead on a clean platinum wire and testing it, when cool, under the lamp, when it should appear purplish white or dull pale purple. It is always advisable to test the bead first in this manner, as, although the reagent may have been proved free from uranium, the platinum wire once contaminated with this element requires very careful cleaning and testing, as described below, in order to remove all traces of the con-

* Also known as a " black lamp." The short-wave ultra-violet lamp. however, is better for making the radio-active minerals themselves fluoresce.

tamination.

A sodium fluoride bead fulfilling the above requirements having been prepared, a very little of the finely-powdered material under test is introduced and strongly heated in the bead for two minutes or more, cooled and viewed under the long-wave lamp. The presence of uranium is indicated by a bright lemon-yellow or bright yellow-green fluorescence. The presence of rare earths tends to quench this fluorescence. Columbium-bearing minerals devoid of uranium give a bead that fluoresces in a much weaker way in a pale, rather dull, yellow colour, but little experience is required to distinguish the uranium fluorescence which is specific.

To clean the platinum wire, the bead is re-melted and flicked off, and the wire heated until all trace of the sodium flame has disappeared. A fresh sodium fluoride bead is then made, flicked off and the wire re-heated until free of sodium. This procedure requires to be repeated at least three and often as many as four times before the ultra-violet lamp shows that a bead is free from all trace of uranium fluorescence.

It will be observed that the foregoing test (*b*) is described as requiring favourable conditions. It is unfortunate that lime interferes very seriously (less so Si, Ti, Fe, and SO_4); as little as 6 per cent. of calcium fluoride in the bead nearly completely extinguishes the fluorescence. Calcium alters the fluorescence to a greenish hue. Nevertheless the test has been applied quantitatively to igneous rocks (J. Hoffman, *Sitzber. Akad. Wiss. Wien*, 1939, **148,** 189; cited also by E. B. Sandell, *Colorimetric Determination of Traces of Metals*, New York, 1944, pp. 435-436) an elaborate separation from interfering elements being necessary.

(*c*) Acid solutions, *e.g.*, those prepared by opening up with hydrofluoric and sulphuric acids for manganese or iron and titania may, on dilution, be tested for uranium fluorescence with a short-wave ultra-violet lamp. This is best carried out in a Pyrex glass beaker.

CHAPTER XI

OCCURRENCE OF THE ELEMENTS

FOR convenience, the elements will be considered in the order in which they are given in a statement of analysis, attention being confined to those which may be sought in the course of rock analysis. On the whole, more attention will be given to the less common and rarer elements since the distribution of the commonest is so universal and well known. The distribution of some of the rarer elements in rocks and minerals is being steadily investigated at the present time, largely by physical methods, including quantitative spectrography and X-ray spectra. First, however, the results of Clarke and Washington's computations* as to the chemical composition of the "ten-mile crust," as calculated from chemical analyses, are given in Table I. In

TABLE I

Oxygen	46.71	SiO_2	59·07
Silicon	27·69	Al_2O_3	15·22
Aluminium	8·07	Fe_2O_3	3.10
Iron	5·05	FeO	3·71
Calcium	3·65	MgO	3·45
Sodium	2·75	CaO	5·10
Potassium	2·58	Na_2O	3·71
Magnesium	2·08	K_2O	3·11
Titanium	0·62	H_2O	1·30
Hydrogen	0·14	CO_2	0·35
Phosphorus	0·13	TiO_2	1·03
Carbon	0·094	P_2O_5	0·30
Manganese	0·09	MnO	0·11
Sulphur	0·052	Rest†	0·44
Barium	0·05		
Remaining elements	0·244		100.00
	100.00		

* *Prof. Paper* 125, *U.S. Geol. Surv.*, 1924, 32.

† "Rest" includes ZrO_2, 0·04 ; Cl, 0·05 ; F, 0·03 ; S, 0·06 ; $(Ce,Y)_2O_3$, 0·02 ; Cr_2O_3, 0·05 ; V_2O_3, 0·05 ; NiO, 0·03 ; BaO, 0·05 ; SrO, 0·02; Li_2O, 0·01 ; Cu, 0·01 ; C, 0·04.

Table II a selection of the results of more recent work is taken from a paper by I. and W. Noddack.*

TABLE II

Expressed in grams per gram of rock in the earth's crust.

H	$8{\cdot}8 \times 10^{-3}$	Cr	$3{\cdot}3 \times 10^{-4}$
Li	5×10^{-5}	Mn	8×10^{-4}
Be	5×10^{-6}	Fe	$4{\cdot}7 \times 10^{-2}$
B	$1{\cdot}4 \times 10^{-5}$	Co	$1{\cdot}8 \times 10^{-5}$
C	$8{\cdot}7 \times 10^{-4}$	Ni	$1{\cdot}8 \times 10^{-4}$
O	$4{\cdot}94 \times 10^{-1}$	Cu	$1{\cdot}0 \times 10^{-4}$
F	$2{\cdot}7 \times 10^{-4}$	Zn	2×10^{-4}
Na	$2{\cdot}64 \times 10^{-2}$	Rb	$3{\cdot}4 \times 10^{-5}$
Mg	$1{\cdot}94 \times 10^{-2}$	Sr	$1{\cdot}7 \times 10^{-4}$
Al	$7{\cdot}51 \times 10^{-2}$	Zr	$2{\cdot}3 \times 10^{-4}$
Si	$2{\cdot}575 \times 10^{-1}$	Mo	$7{\cdot}2 \times 10^{-6}$
P	$1{\cdot}2 \times 10^{-3}$	Ba	$4{\cdot}7 \times 10^{-4}$
S	$4{\cdot}8 \times 10^{-4}$	Pt	2×10^{-7}
Cl	$1{\cdot}88 \times 10^{-3}$	†Pb	8×10^{-6}
K	$2{\cdot}4 \times 10^{-2}$	Bi	$3{\cdot}4 \times 10^{-8}$
Ca	$3{\cdot}4 \times 10^{-2}$	Th	$2{\cdot}5 \times 10^{-5}$
Ti	$5{\cdot}8 \times 10^{-3}$	U	$5{\cdot}0 \times 10^{-6}$
V	$1{\cdot}6 \times 10^{-4}$		

Somewhat more recently V. M. Goldschmidt (*J. Chem. Soc.*, 1937, p. 656) has given the following data (Table III) as to the abundance of the elements in the earth's crust. It is based partly upon the pioneer work of Clarke and Washington, and partly upon later investigations with regard to rare elements made at the Universities of Göttingen and Oslo, by von Hevesy and his co-workers, and by I. and W. Noddack.

Additions to our knowledge of geochemistry are accumulating at an ever-increasing rate, but the most outstanding contribution has been that of the late Professor V. M. Goldschmidt and his co-workers when he enunciated (*J. Chem. Soc.*, 1937, pp. 655-673) the guiding principles underlying the distribution of chemical elements in minerals and rocks.

Goldschmidt's first principle was that the partition of elements between a metallic (iron-nickel) liquid, rich in free electrons, a sulphidic liquid of a semi-metallic nature,

* *Angewandte Chemie*, 1936 (January 4), p. 2.

† For the distribution of lead, thorium, and uranium in the various rock types see communications from G. Hevesy and R. Hobbie, and A. Holmes in *Nature*, December, 19, 1931, **128**, 1038-1040.

TABLE III

ABUNDANCE OF ELEMENTS IN EARTH'S CRUST

(*Expressed in grams per ton*)

Li	65	Pd	0·01
Be	6	Ag	0·1
B	3	Cd	0·5
O	494,000	In	0·1
F	270	Sn	40
Na	28,300	Sb	1_2
Mg	21,000	I	0·3
Al	88,200	Cs	7
Si	276,000	Ba	390
P	786	La	19
S	500	Ce	44
Cl	480	Pr	5·6
K	25,900	Nd	24
Ca	36,300	Sm	6·5
Sc	5	Eu	1·0
Ti	6,300	Gd	6·3
V	100	Tb	1·0
Cr	200	Dy	4·3
Mn	930	Ho	1·2
Fe	51,000	Er	2·4
Co	40	Tu	0·3
Ni	100	Yb	2·6
Cu	100	Cp(=Lu)	0·7
Zn	40	Hf	3·2
Ga	15	W	69
Ge	7	Re	0·001
As	5	Ir	0·001
Se	0·6	Pt	0·005
Rb	310	Au	0·005
Sr	420	Hg	0·5
Y	31	Tl	0·3
Zr	190	Pb	16
Cb	15	Bi	0·2
Mo	15	Th	11
Rh	0·001	U	4

and an ionic (silicate) liquid afforded a classification into three groups of elements in agreement with their geochemical affinities. A fourth group comprised the elements that are accumulated in gas phases, either as free volatile elements or as gaseous compounds. A fifth group contained those elements that are concentrated by living organisms in later stages of terrestrial evolution. These divisions are connected with potentials of ionization and the type of ionic structure, but they likewise account for the scarcity of certain elements in the earth's crust. Thus those elements that are rare in the earth's silicate crust are largely present in the first two groups or else among the rare gases of the

fourth group, *i.e.*, either below the silicate crust or above it. This also explains the higher content of precious metals, germanium, etc., in meteoric irons as compared with rocks of the earth's crust.

Next Goldschmidt considered the principles guiding the formation of crystalline minerals. The entry of atoms or ions into a crystal depends on the size (*i.e.*, radii) of the individual atoms or ions; only those particles can enter that are of a size appropriate to the lattice spacings. Thus the growing crystals act as a kind of sorting or sieving mechanism. It followed, therefore, that one of the most important principles controlling distribution of the elements was their grading according to size, especially as compared with the lattice spacings or interatomic distances of rock-forming minerals of the most common elements.

Professor H. H. Read,* referring to the mineral transformations that take place during such processes as granitization and metamorphism, has recently suggested that the large oxygen atoms of the silicate lattice remain more or less in position whilst the small migrating atoms drift through.

TABLE IV

ATOMIC RADII

(A). Arranged according to increasing radius.

Radius, Å.	*Ions.*	
0·1 - 0·3	B^{3+}, C^{4+}, N^{5+}, S^{6+}	
0·3 - 0·5	Be^{2+}, Si^{4+}, Ge^{4+}, P^{5+}, V^{5+}, Mo^{6+}, W^{6+}	
0·5 - 0·7	Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Ti^{4+}, Cb^{5+}, Ta^{5+}	
0·7 - 0·9	Li^{1+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Sc^{3+}, In^{3+}, Zr^{4+}, Hf^{4+}, Sn^{4+}	Mn^{2+}
0·9 - 1·1	Na^{1+}, Ca^{2+}, Cd^{2+}, Y^{3+}, Gd^{3+}—Cp^{3+}, Ce^{4+}, Th^{4+}, U^{4+}	
1·1 - 1·4	K^{1+}, Sr^{2+}, La^{3+}—Eu^{3+}	
1·4 - 1·7	Rb^{1+}, Tl^{1+}, Cs^{1+}, Ba^{2+}, Ra^{2+}	

(B). Arranged according to valency and increasing radius.

Monovalent ions :	Li 0·78, Cu 0·96, Na 0·98, K 1·33, F 1·33, Cl 1·81
Divalent ions :	Be 0·34, Mg 0·78, Ni 0·78, Cu 0·80, Co 0·82, Fe 0·83, Zn 0·83, Mn 0·91, Cd 1·03, Ca 1·06, Hg 1·12, Pb 1·32, O 1·32, Ba 1·43
Trivalent ions :	Al 0·57, Cr 0·64, Fe 0·67, Mn 0·70
Quadrivalent ions :	Si 0·39, Ti 0·64, Mo 0·68, W 0·68, Zr 0·87, V 1·05

The measurements are given in Ångstrom units (1 Å $= 10^{-8}$ cm.) and the figures are taken from the works of V. M. Goldschmidt and W. L. Bragg.

* Q.J.G.S., 1948, **104**, p. 180.

Commenting on the table of ionic radii (Table IV), W. L. Bragg* says " A striking feature of this list, which has an important application to the structure of minerals, is the large size of the oxygen ion as compared with that of the common cations such as Na, Mg, Fe, Al, Si . . . . It is so large that the packing together of the ions in the structures is mainly a packing of the oxygen ions, with the metallic cations in the interstices."

Given a table of radii of ions, it is usually possible to predict into which minerals any given element will enter. Thus we may anticipate a connection between magnesium and a number of other elements :— Mg^{2+} 0·78, Li^{1+} 0·78, Ni^{2+} 0·78, Fe^{2+} 0·83, Co^{2+} 0·83, Sc^{3+} 0·83. In the pair Mg-Ni the radii are alike, and so are the charges, both metals being bivalent. Consequently Ni ions pass into the crystals of magnesium silicate with about the same probability as the Mg ions ; as a result, the amount of nickel in a number of magmatic minerals is roughly proportional to the magnesium present. If radii, charges, and the ionic type of two elements are exactly alike or very similar, then no separation takes place at all, as in the pairs zirconium-hafnium and yttrium-holmium. That is why the second element of each of these pairs is hidden away in the more common element forming the first of each of these pairs.

When there is a small difference of ionic radius, entry into the lattice is more difficult for the larger ion, and conversely exit more easy. This latter results in a lower melting point for the member of a mineral series in which the larger ion is most abundant. Thus the melting point of iron olivine (Fayalite Fe_2SiO_4. M.P.1205°C.) is lower than that of magnesium olivine (Forsterite Mg_2SiO_4. M.P. 1910°C.), and the larger ion is concentrated relative to the smaller ion in the later stages of magmatic crystallization. Quite small differences in radii thus lead to enrichment of certain components at late stages in crystallization. Thus we find considerable amounts of rubidium, caesium, and thallium in certain late-crystallized, pegmatitic, potash felspars, the relation of the radii of these univalent ions being :—

* The Atomic Structure of Minerals, 1937, p. 31.

K 1·33 Å., Rb 1·49 Å., Tl 1·49 Å., Cs 1·65 Å.

A crystal may extend its hospitality to ions having a fitting radius but a different charge though, of course, of the same sign. Expressed in another way, a crystal lattice may accommodate ions having a fitting radius though of a different valency; for instance, magnesium minerals may take up scandium or lithium. The ion which has a larger charge has the preference over other ions of the same size but of lower charge. Thus the atoms of scandium enter into early crystallization of magnesium minerals, especially into the pyroxenes of gabbros and basalts. To take an example of the greatest importance to the petrologist, in the lime-soda felspars (the plagioclases) the bivalent calcium ions preferentially enter the crystal :—

Anorthite	Ca^{2+} $(Al_2\,Si_2O_8)^{2+}$	M.P. 1550° C.
Albite	Na^{1+} $(Al\,Si_3O_8)^{2+}$	1090° C.

As a result calcium is concentrated in early fractions of plagioclase crystals, and sodium in the later fractions. In the same way strontium and barium enter early crystals of potash felspars. Correspondingly, ions of fitting radius, but having a lower charge are admitted only reluctantly, owing to correspondingly weakened electrostatic bonds, and are consequently concentrated in late crystallates. Thus lithium is concentrated in the last crystallates of magnesium minerals. The controlling factor, therefore, is the ionic potential, given by the quotient between ionic charge Z and ionic radius r $\left(\frac{Z}{r}\right)$

The application of the foregoing rules enables us to discriminate between elements of early and those of late introduction into the crystals of common rock-forming minerals, as is well exemplified by the following examples given by Goldschmidt :—

	Early				Late			
	Cr_2O_3 %	NiO %	CoO %	MgO %	BaO %	Cb_2O_3 %	La_2O_3 %	K_2O %
Peridotite (dunite)	0·50	0·40	0·03	40	0·0003	—	—	0.1
Gabbro	0·05	0·02	0·01	8	0·007	0·001	0·001	1
Diorite	0·01	0·005	0·004	3	0·03	0·003	0·003	2
Granite	0·0003	0·0003	0·001	1	0·05	0·005	0·005	4
Nepheline Syenite	0·0001	0·0003	0·001	1	0·06	0·02	0·05	6

The enunciation of these principles by Goldschmidt has truly cast a flood of light and understanding on what was formerly a seemingly disconnected series of geochemical facts. It has indeed done more than that: it has made possible the prediction of hitherto unknown facts. Thus the systematic investigation of the minor constituents of magmatic minerals and rocks has greatly augmented our knowledge of geochemistry. (For a discussion on the order of abundance of elements in the earth's crust as influenced by ionic size and charge see J. H. Pannell, *Amer. Min.*, 1943, **28**, 605-613).

In order to understand further the presence of one or more minor elements in the commoner rock-forming minerals, it is necessary to know something of the structures of these minerals, and, in view of the large size of the oxygen ion compared with the common cations such as Na, Mg, Fe, Al, Si, etc., the packing together of the ions in the structures is mainly a packing of the oxygen ions, with the metallic cations in the interstices. (See W. L. Bragg, *The Atomic Structure of Minerals*, 1937). It appears that Fe, Co, Ni, Mg, etc., require to be surrounded by six oxygen atoms; Al and Si are surrounded by four only; large ions such as K, Na, Ca, and Ba require from seven to twelve oxygen atoms. In addition to the principles of replacement of ions already mentioned, a further implied condition is that the positive and negative valencies throughout the structure must balance; there must be a neutral total charge on the lattice.

The pyroxene structure consists of single chains of (SiO_3) groups, while in the amphibole structure the chains are double with (Si_4O_{11}) groups, the chains in both structures being bound together by the metallic cations. The atomic, as distinct from the older molecular, formula for diopside is thus $Ca\ Mg\ (SiO_3)_2$, and for tremolite is $(OH)_2\ Ca_2\ Mg_5\ Si_8\ O_{22}$. From these basic types, by replacement of part of the Si by Al, and part of the Mg by Fe, the more complex members of the pyroxenes and amphiboles are derived. Thus in tremolite the two Ca ions are large while the five Mg ions are small. Reference to the table of ionic radii shows that cations of a suitable size to replace Mg are Fe, Co, Ni,

Zn, and Cu. It is indeed a fact that many analyses of amphiboles and pyroxenes have recorded traces of Zn and Cu. To quote what is probably an extreme case, an amphibole from Franklin Furnace, New Jersey, contains 4·70 per cent. ZnO.* Cu seems to prefer the amphiboles and pyroxenes to olivine.

The olivine structure, consisting of separate (SiO_4) groups packed closely together with Mg atoms between six oxygen atoms, is a much simpler one. Not only is the Mg most readily replaced by Fe, but analyses usually show Ni and Cr. The presence of Co may be anticipated.

The mica structure consists of hexagonal sheets of linked silicon-oxygen tetrahedra. Muscovite consists of two of these sheets placed together with the vertices of the tetrahedra pointing inwards and linked together by Al ions ; in biotite the linkage is by means of Mg and Fe ions. Pairs of these double sheets are in turn linked together by large ions, such as K, surrounded by twelve oxygen ions. In such a structure there is considerable scope for replacement ; not only are the large ions K, Ca, and Na interchangeable, but there are numerous possibilities for the small ions to join the single sheets, as chemical analyses bear witness.

Felspars consist of a framework of linked SiO_4 and AlO_4 tetrahedra with the cations, K, Na, Ca, or Ba in the interstices. The possibilities for ionic interchange are considerably reduced, for there are no spaces for small ions such as Fe, Cr, Mn, etc., which, in any case, require a situation within an octahedral group. In the case of quartz, which consists of tetrahedral groups of oxygen atoms surrounding a central silicon atom, there is no possibility of replacement.

The former conception that very minute quantities of the rare elements are dispersed in the earth's crust in a haphazard manner has now to give place to a more orderly picture of the distribution of these elements, which are very much more common than was formerly believed. The factors influencing this systematic geochemical behaviour have recently been conveniently summarized by L. H. Ahrens† as follows :—

* W. F. Foshag, *Amer. Min.*, 1936, **21**, 63-67.
† *Trans. Geol. Soc.*, S. Africa, 1946, **48**, 207-231.

"(1) The general chemistry of the elements in question.

(2) Ionic size and isomorphism. Apart from the influence the radius of an ion has on regulating crystal chemistry, it also affects the general chemistry of an element. Under this sub-heading, however, the effects of ionic size on geochemistry are restricted to the 'mechanical aspect,' that is, the sizes of the ions and their influence on isomorphic behaviour.

(3) Radioactivity, which must also be taken into account, since certain atomic species have originated from a process of atomic decay. For example, lead in uranium and thorium minerals is largely radiogenic, as is also the strontium of lepidolites, the progenitor in the latter case being the rubidium isotope of mass number 87."

Thus geochemistry no longer depends mostly on descriptive mineralogy and the data derived from chemical analyses of rocks and minerals, but is now firmly based on the development of atomic physics and the laws of crystal chemistry. The laws of atomic lattices explain such well-known associations in economic geology as Cu, Co, Ni, and especially Cu and Fe ; Zn, Fe, Mn ; constant presence of Au in Ag ; Cd and In ; the Pt group with Fe, Cu, As, and Mo ; etc.

For an example of the practical applications of these principles the reader is referred to a paper by Prof. L. R. Wager and Dr. R. L. Mitchell, "Preliminary observations on the distribution of trace elements in the rocks of the Skaergard intrusion, Greenland," *Mineralog. Mag.*, 1943, **26,** 283-296.

Before ending this review of some of the guiding principles of geochemistry, there is one more aspect that was emphasized by V. M. Goldschmidt, *viz.*, the concentration of certain elements by living organisms, particularly plant life. Certain marine organisms have the power of accumulating copper and vanadium ; likewise the presence of iodine in seaweed is well-known. Some very remarkable concentrations of elements are associated with the natural hydrocarbons, especially in such naturally occurring non-volatile residues from petroleum as bituminous rocks. The accumu-

lations of V, Mo, and Ni in such bitumens and asphalts, Goldschmidt suggested, was due to their having facilitated reactions between sulphuretted hydrogen and organic substances leading to the production of hydrocarbons. Their catalytic action having been fulfilled, these elements doubtless formed organo-metallic compounds and migrated together with the hydrocarbons. When the hydrocarbons lost their volatiles, these metallic elements were concentrated in the non-volatile residuals.

Plant life has the capacity of extracting some elements from the soil. These become concentrated in the resulting humus and upper soil layers. Fossil humus, such as coal and lignite, is similarly enriched in many rare elements; in fact nearly all rare elements are concentrated in certain coal ashes.

That geochemical studies are not without their industrial significance is shown by the commercial extraction of vanadium from soot resulting from certain petroleums and from certain petroleum cokes; of germanium from flue dusts resulting from certain coals; and of gallium from bauxite containing about 1 oz. to the ton, the last-mentioned being coupled with the production of aluminium. Such studies also have an important bearing on agriculture and stock-raising. Furthermore, the concentration by vegetation of sub-surface elements in the soil or humus, or in the vegetation itself, is now being investigated as a biogeochemical means of prospecting for mineral deposits.

Silicon.—This is a most ubiquitous constituent, occurring to a greater or less extent in almost all rocks, minerals, and natural waters, as well as a great many artificial products. In the realm of natural products it is difficult to cite cases with certainty where silicon will not be present either as silica or silicate; indeed, after oxygen it is the most abundant element of the lithosphere.

Titanium.—The distribution of titanium amongst natural products is almost as universal as silicon, though in smaller quantity, it being placed ninth by Clarke and Washington (*op. cit.*) in the order of abundance of constituents in the upper ten miles of the lithosphere. Wherever silicon is, there also will titanium be found, and it is probable that in

the mineral kingdom there are very few exceptions, if any.

Among igneous rocks it is decidedly more abundant in those with less than 50 per cent. silica, where it frequently rises above 1 per cent. and may reach 5 per cent. in many basic rocks, particularly the basic alkaline types. Many basalts and intrusive "greenstones" contain several per cent. of titania, and the average in ten analyses of camptonite (Osann) is 3·86 per cent. In melilite-basalts and some nephelinites the titania content may be in the neighbourhood of 5 per cent. Titania is unusually abundant in the volcanic rocks flanking Ruwenzori, Toro District, Uganda, particularly in bombs from the Katwe crater.* Clarke and Washington (*op. cit.*, p. 104) have shown that titanium tends to be plentiful in sodic rather than potassic rocks and in those with much iron rather than magnesium. In general, titanium is lowest in the highly siliceous and felspathic rocks; thus in the averages quoted by R. A. Daly† the following titania figures are the lowest for igneous rocks: alaskite 0·07 per cent., alkaline granite 0·11 per cent., lherzolite 0·12 per cent., anorthosite 0·15 per cent.

In sedimentary rocks titanium is equally important, though its amount is generally dependent on the titanium content of the distributive province in each case. The titanium content rises very high locally in black sands where iron ores are concentrated. The high titanium content of clays is sometimes ascribed to the refractory nature of titanium minerals whereby they tend to become concentrated in residual products.‡ No doubt this is part of the explanation, but there are two other important factors: (*a*) the ubiquity of minute rutile inclusions in mica so that flakes containing them may be deposited in the finest sediments; (*b*) the tabular and platy habit of many anatase crystals giving them greatly increased buoyancy in water.

The importance of the frequent occurrence of rutile in minute needles and the buoyancy imparted to them when they are inclosed in microscopic flakes of mica, sericite, etc.,

* A. Holmes and H. F. Harwood; The Volcanic Area of Bufumbira. Geol. Survey Uganda, Memoir III, Part II, 1937, p. 30.

† "Igneous Rocks and their Origin," New York, pp. 24-36.

‡ Hillebrand-Lundell ("Applied Inorganic Analysis"), New York, 1929, p. 452.

is borne out by the general occurrence of titanium in analyses of mineral dust. In ten analyses made by the author of mineral dust from silicotic human lungs, the content of TiO_2 varied from 0·08 per cent. to 1·00 per cent. and averaged 0·56 per cent.

The titanium content of laterites and bauxites is usually quite appreciable.

Titanium is an essential constituent of the following rock-forming minerals : rutile, anatase, brookite, ilmenite, titanomagnetite, sphene and its decomposition product leucoxene, perovskite, schorlomite, and pseudobrookite. In addition it is usually an important constituent of many pyroxenes (both orthorhombic and monoclinic), amphiboles, micas (particularly biotite), garnets, and other ferro-magnesian minerals. Analyses of magnetite and hæmatite sometimes show appreciable titanium ; such magnetite is termed titanomagnetite and may contain up to 25 per cent. TiO_2. In addition there are several other titaniferous species or sub-species of which the best examples are titan-augite, titaniferous melanite, and schorlomite. These last three are all characteristic of alkaline rocks. Melanite is practically confined to nepheline-syenites, phonolites, leucitic and nephelitic lavas ; it is frequently titaniferous, and when the titania content is very high it graduates towards schorlomite $3CaO.(Fe,Ti)_2O_3.3(Si,Ti)O_2$. An analysis of schorlomite from Magnet Cove, Arkansas, shows 21 per cent. TiO_2. Melanite from Perlerkopf (Eifel) and Oberrotweil contains 8·3 and 12·10 per cent. TiO_2 respectively, while iivaarite (a variety of schorlomite) from the latter locality contains even more TiO_2.*

Titaniferous augite has a very characteristic appearance and pleochroism under the microscope which distinguishes it from other pyroxenes. Titaniferous augite separated from the ilmenite gabbro of Azhinsk, Western Siberia, contains 9 per cent. TiO_2.† Ordinary augite commonly contains up to 3 per cent. TiO_2. Hornblende often contains several per cent. of TiO_2, and cases have been recorded

* O. Zedlitz, *Zentr. Min. Geol.*, 1933, A, 225-239.

† P. I. Lebedev and A. P. Lebedev, *Comp. rend. Acad. Sci. U.R.S.S.*, 1934, **3**, 294-300.

with 8 and 10 per cent. The titaniferous hornblende kaersutite is thought to be characteristic of the petrographical provinces of Tertiary alkali effusive rocks. Kaersutite from a teschenite dyke on the island of Dogo, Oki Islands, Japan, contained 7·00 per cent. TiO_2.* Olivine has, as a rule, very little titanium, in accordance with the generalization of Clarke and Washington given above. Titanolivine was a misnomer, it being a variety of clinohumite which may contain 5-6 per cent. TiO_2. Alleghanyite (*Mineralog. Mag.*, 1944, **27**, 44) affords further evidence of the ability of the humite family to accommodate Ti.

ALUMINIUM.—Aluminium is the most abundant of the metals and comes third after oxygen and silicon on Clarke and Washington's list of elements of the lithosphere and second on the list of oxides. It is an essential constituent of most rocks and many minerals but, owing to the ease with which it is oxidized, it never occurs native.

Considerable amounts of aluminium will be encountered in the analysis of bauxites, many refractories, clays, bricks, cement, etc. The mineral dust from silicotic human lungs usually contains 10-20 per cent. Al_2O_3. In the analysis of minerals aluminium will frequently be found even though it is not usually expressed in the formula — *e.g.*, hypersthene often contains several per cent. of Al_2O_3.

IRON.—After aluminium, iron is the next element in order of abundance in the outer portion of the lithosphere, but, taking the earth as a whole, it is probably the most abundant metal. It occurs in both the bivalent (ferrous) and trivalent (ferric) states in practically all rocks, hundreds of minerals, and is the principal constituent of the majority of meteorites.

Iron rarely occurs native, but its occurrence in segregations in some of the basalts of Greenland is well known — *e.g.*, a mass of iron weighing twenty-five tons is recorded from the island of Disko. The bulk of the evidence, however, goes to show that this is a kind of geological accident or freak due to the basalts intruding bituminous sediments from which they have absorbed carbonaceous matter with consequent reduction of ferrous iron to the metal while the rock was still molten. The iron is described by Sir Harold

* T. Tomita, *J. Shanghai Sci. Inst.*, Sect. 2, 1934, **1**, 99-136.

Carpenter as a high-carbon, nickel-cobalt steel which displays a structure due, probably, to the action of carbon or carbon monoxide on metal at about 900° C.*

In the great majority of rocks ferrous iron is in considerable excess of ferric iron. It has, however, been shown by H. S. Washington† that whereas in the majority of glassy lavas FeO is higher than Fe_2O_3, the reverse is often the case in holocrystalline lavas of the same general composition and from the same volcano. Likewise ferric iron is frequently found in minerals generally supposed not to contain it — *e.g.*, olivine frequently contains 2 per cent. Fe_2O_3 and hypersthene 2-3 per cent. Fe_2O_3. The proportion of ferrous iron to ferric iron is in some cases a deciding factor between different members of isomorphous series — *e.g.*, biotite and lepidomelane, almandine and andradite.

MANGANESE.—Manganese comes thirteenth in the Clarke-Washington lists, both of elements and oxides. The MnO content of the great majority of silicate rocks lies between 0·05 per cent. and 0·20 per cent., the higher figure being encountered in the more basic rocks. It is held principally by the various ferromagnesian minerals, pyroxenes, amphiboles, garnets, olivines, and micas, etc., which yield correspondingly high figures. Nevertheless, it is the more ferriferous members of each isomorphous ferromagnesian series which carry manganese in greatest amount, apart from actual manganese minerals. While 0·3-0·4 per cent. MnO are common figures for augite, in ægirine-augite and ægirine with high iron the MnO content rises to 1-2 per cent. Common hornblende usually contains from a few tenths of 1 per cent. up to 2 per cent. of MnO. Garnets frequently contain a considerable amount of MnO, the content varying from 0·1 to nearly 43 per cent., the theoretical amount for the manganese garnet spessartite. In olivines, MnO may reach 2 per cent., tending to rise from the forsterite $2MgO.SiO_2$ to the fayalite $2FeO.SiO_2$ end of the series. In the micas, MnO may be anything up to 2 per cent., but in the iron-rich micas — lepidomelane — it may reach 4 per cent. Among the epidotes, piedmontite is a variety containing

* *Nature*, London, 1935, **136**, 152-153.
† *Am. Journ. Sci*. 1920, **50**, 458.

considerable trivalent manganese — up to 15 per cent. or more of Mn_2O_3 Thulite is a manganiferous variety of zoisite. Manganese also enters to a small extent into the composition of many other rock-forming silicates — *e.g.*, staurolite, tourmaline, chlorite, etc. Rhodonite, the manganese metasilicate, contains 54·1 per cent. MnO, but is practically confined to the neighbourhood of manganese ores and metamorphosed manganiferous rocks.

The manganese content of shales and phyllites is often higher than that of most rocks. The assimilation of shale by granite or diorite may lead to enrichment in manganese which appears to be largely concentrated as the spessartite molecule in the garnets thus produced. In the case of the Dartmoor granite the MnO content of the garnet rises to over 20 per cent. and is greatest in garnet from the highest levels of the granite, where presumably assimilation has been greatest.*

Manganese also occurs in rocks to some extent (particularly along cracks and joints) as the oxides, hydrated oxide, hydroxide, and carbonate — pyrolusite, manganite, psilomelane, rhodochrosite. There can be little doubt that many of the high figures for manganese given in the older analyses were due to analytical errors.

MAGNESIUM.—Magnesium, another of the more abundant metals, takes sixth place in the Clarke-Washington list of oxides and eighth among the elements. It is present in almost all igneous rocks, where it usually enters one or more of the ferromagnesian minerals. In addition to silicates it enters spinel $MgO.Al_2O_3$, dolomite $CaCO_3.MgCO_3$, magnesite $MgCO_3$, brucite $Mg(OH)_2$, periclase MgO, together with some less common minerals, all of which may occur in rocks — mostly sedimentary — in company with silicates.

Amongst the silicates, those carrying the largest amount of magnesium are forsterite, enstatite, monoclinic pyroxenes rich in the diopside molecule, tremolite, phlogopite, biotite, serpentine, and talc.

CALCIUM.—Calcium is one of the most widespread metals, coming fifth on the list of elements but third among the oxides of the outer lithosphere. It is an essential constitu-

* A. Brammall and S. Bracewell, *Nature*, 1933, 131, 250.

ent of a great many rock-forming minerals of which some of the principal non-silicate species are calcite $CaCO_3$, aragonite $CaCO_3$, gypsum $CaSO_4.2H_2O$, anhydrite $CaSO_4$, fluor CaF_2, apatite $Ca_4(CaF)(PO_4)_3$, perovskite $CaTiO_2$. Among common rock-forming silicate minerals carrying the most lime are wollastonite $CaSiO_3$, diopside $(Ca,Mg)SiO_3$, the basic plagioclases (rich in the anorthite molecule $CaO.Al_2O_3.2SiO_2$), sphene $CaTiSiO_5$, epidote $(Ca_2(Al,Fe)OH)(Al,Fe)_2(SiO_4)_3$, amphiboles, the lime-alumina and lime-iron garnets grossularite and andradite, and the scapolites.

Calcium also enters many minerals in which it is not regarded as an essential element. Thus pyroxenes which have been described as hypersthene may contain up to 10 per cent. CaO, and variable amounts of CaO in excess of the requirements of the P_2O_5 for apatite are usually found in micas.

Sodium and Potassium.—The two principal alkali metals take sixth and seventh places on the Clarke-Washington list with 2.75 per cent. and 2·58 per cent. respectively. They are essential to several of the most ubiquitous groups of rock-forming minerals—*viz.*, albite, $Na_2O.Al_2O_3.6SiO_2$, orthoclase $K_2O.Al_2O_3.6SiO_2$, the plagioclases m $Na_2O.Al_2O_3.6SiO_2$ n $CaO.Al_2O_3.2SiO_2$, micas (both potash and soda), leucite $K_2O.Al_2O_3.4SiO_2$, nepheline $Na_2O.Al_2O_3.2SiO_2$, the amphiboles (mainly sodium). The presence of abundant sodium in a rock gives rise to the development of sodic types of pyroxenes (ægirine-augite, ægirine, acmite), and amphiboles (glaucophane, riebeckite, arfvedsonite, barkevikite, katoforite, cossyrite, jadeite, etc.) which are very characteristic under the microscope. The sodic pyroxenes contain the acmite molecule $Na_2O.Fe_2O_3.4SiO_2$; the corresponding amphiboles contain the jadeite $Na_2O.Al_2O_3.4SiO_2$ (itself a pyroxene) and / or riebeckite $Na_2O.Fe_2O_3.2SiO_2.FeSiO_3$ molecules.

Other common rock-forming minerals in which sodium is an essential constituent are crocidolite (a soda amphibole), anorthoclase $(Na,K)AlSi_3O_8$, cancrinite $H_6Na_6Ca(NaCO_3)_2$-$Al_8(SiO_4)_9$ analcite $NaAlSi_2O._6H_2O$, sodalite $(Na_4(AlCl)$-$Al_2(SiO_4)_3$, haüyne $(Na_2,Ca)_2(NaSO_4.Al)Al_2(SiO_4)_3$, nosean $Na_4(NaSO_4.Al)Al_2(SiO_4)_3$, melilite $Na_2(Ca,Mg)_{11}(Al,Fe)_4$-

$(SiO_4)_9$, and the scapolites. Soda, and potash too, are present in many of the zeolites. Additional rock-forming minerals in which potassium is essential are glauconite, celadonite, anorthoclase, and kaliophyllite $K_2O.Al_2O_3$.-$2SiO_2$.

Small amounts of alkalis will be found in a great many minerals where they are not essential constituents. On account of the sericite present, the mineral dust from silicotic human lungs may contain up to 5 or 6 per cent. K_2O.

PHOSPHORUS.—It is probably true to say that phosphorus is scarcely ever absent from rocks, where it is essential to apatite, monazite, xenotime, and a number of comparatively rare rock-forming phosphates. Phosphorus is absent, however, from saxonite, harzburgite, lherzolite, and chrome-diopside inclusions from kimberlite pipes.* In igneous rocks the quantity of P_2O_5 usually lies between 0·10 and 0·5 per cent., though it may sometimes rise to 1 per cent. and occasionally to several per cent. The Clarke-Washington average is 0·30 per cent. P_2O_5. As a general rule, phosphorus is higher in the more basic rocks, and favours those with high lime and iron rather than high magnesia, and this generalization is equally applicable to the occurrence of apatite. Phosphorus is locally very abundant in biotite-pyroxenite.†

Apatite occurs in two species, fluor-apatite $(3CaO.P_2O_5)_3$.-CaF_2 and chlor-apatite $(3CaO.P_2O_5)_3.CaCl_2$, and mixtures of the two. Fluor-apatite is much more abundant than chlor-apatite. Monazite $(Ce,La,Di)PO_4$ and xenotime YPO_4 are more or less restricted to granites and diorites and their gneissic equivalents, but much larger developments of these minerals occur in pegmatite veins, particularly syenite-pegmatites.

In sedimentary rocks the content of phosphorus rises greatly in phosphate rocks, phosphatic nodules, and bone-beds. Since phosphorus is an essential constituent of the human body, a mineral residue from silicotic lungs usually

* Analyses 3,4,5,7 by L. S. Theobald in "A Contribution to the Petrology of Kimberlite and its Inclusions" by A. Holmes, *Trans. Geol. Soc., S. Afr.*, 1937, **39**, 379-427.

† Doris L. Reynolds, *Min. Petr. Mitt*, 1935, **46**, 450-452; see also analyses C', 7, & 11, pp. 30-31, in *Uganda Geological Survey, Memoir III*, Part II, 1937, by A. Holmes and H. F. Harwood.

contains from 2-10 per cent. P_2O_5.

Phosphorus will be found, usually to the extent of a few tenths of one per cent., in most rock-forming minerals, however carefully they have been separated. This is usually attributed to the occurrence of microscopic inclusions of apatite; phosphorus, however, has the correct radius and co-ordination to replace silicon, and it is possible that future work may prove that it does.

HYDROGEN.—As the free gas, hydrogen has been found in very minute amounts in certain granites and other rocks, but as water or hydroxyl groups it will almost invariably be present in rocks and minerals. Water may be present, either in the free state or chemically combined, in one or more of the constituent minerals. The degree of firmness with which the combined water may be held varies greatly, for while some zeolites give off their water with the greatest ease, certain other minerals part with very little of their water at temperatures approaching 1,000° C. It has also been shown that moisture is adsorbed during the process of crushing and grinding, and that this adsorption increases with further grinding. Atmospheric conditions at the time of pulverization of the sample will have an influence on the amount of moisture adsorbed. Very fine ($<1\mu$) powders of silica-glass, orthoclase, muscovite, etc., are highly hygroscopic.*

For analytical purposes, a rough discrimination between combined and uncombined water is made by returning the amount given off up to 110° C. and that released at higher temperatures (see Chapter VI). While some of the more loosely combined water of the zeolites and some other minerals may be included in the H_2O–110° C., in the majority of rocks and minerals this error in discrimination between combined and uncombined water will not be very serious. In the analysis of minerals (and some clays), the presence of several hydroxyl groups can be demonstrated by preparing a dehydration curve, when each hydroxyl group gives rise to a peak. An example is afforded by the studies of Tsurumi and Yoshiki on the lepidomelane of Ishikawa, Japan. Their chemical analysis approximates to the formula $(Si,Al)_4$-

* O. Tamm, *Arkiv. Kemi. Min. Geol.*, 1934, **11**, No. 14.

$(Mg,Fe,Al,Mn,Ti)_{3\cdot4}(K,Na)(OH,F)_3$. Their graph showing change of weight with temperature from 25° to 1,000° C. shows three breaks at 260°, 510°, and 630° C., with similar discontinuities in the change of refractive index and optic axial angle with temperature. The physical changes suggest that the chemical analysis is correct in indicating three hydroxyl groups instead of the more usual two.* Comparison of dehydration curves of bauxites with the curves characteristic of diaspore, gibbsite, kaolinite, limonite, etc., considered in conjunction with the chemical analyses, may assist in determining the principal minerals present.†

The problem of discrimination between adsorbed moisture and essential or hydroxyl water has become prominent in recent years on account of modern methods of recalculation of mineral analyses of silicate minerals in accordance with the results of X-ray work. It was soon discovered that it is not correct to calculate analyses to a " dehydrated " basis, *i.e.*, leaving H_2O and F out of account. This makes it important in high-class mineral analyses to make a serious attempt to sub-divide the total water into adsorbed and essential water. While it may rarely be possible to execute a properly regulated dehydration curve, there should be no difficulty in carrying the " H_2O- " on to two or three higher temperatures — say 150, 200, and 250° C. approximately. If the loss at 250° C. is but little more than at 110° C., then the whole loss at 250° C. is almost certainly hygroscopic.

Dr. M. H. Hey has expressed the problem thus‡ : " By far the most troublesome constituent of minerals for the satisfactory presentation of a chemical analysis is water, since it may be present adsorbed, when it constitutes an impurity, or as hydroxyl groups, or as molecular water of crystallization, and the accurate distinction of the three forms is rarely possible. As a general rule, small quantities of water lost at a low temperature may be assumed to be adsorbed, but the distribution of water into impurity and constitutional (including water of crystallization) is often essentially arbitrary and constitutes the most serious weak-

* S. Tsurumi, *Proc. Imp. Acad. Tokyo*, 1933, **9**, 320-323 ; B. Yoshiki, *ibid.*, pp. 324-326.

† J. Györki, *Földtani Közlöny*, Budapest, 1931, **61**, 64-67.

‡ *Mineralog. Mag.*, 1939, **25**, 404.

ness in the determination of empirical cell contents." The suggestion is made in the same paper that a distinction between these three forms of water might be obtained by the use of deuterium oxide (*op. cit.* p. 408).

The problem assumes still greater importance in studies of the clay minerals. In these the problem is twofold: one is the adsorbed water, particularly the interlayer water between the lattice sheets, which is closely related to exchangeable bases; the other is the so-called high temperature water or hydroxyl, which is an essential part of the crystal lattice. Here determination of the two types of water involves quite different methods of study: the adsorbed or interlayer water is best investigated by means of differential thermal analysis,* whereas the essential or hydroxyl water is best indicated by plotting retention of water against change in temperature, *i.e.*, by dehydration curves.† There is, however, some question about determination of the hydroxyl water from dehydration curves.‡

The water given off by rocks on ignition may vary from a half per cent., sometimes less, up to about 10 per cent. High water content in the case of an igneous rock may be due to decomposition by weathering, or hydrothermal action, with the production of hydrated products from the original "dry" minerals; on the other hand, a large proportion of the primary minerals may contain hydrogen. The water in the first case, however, is usually more easily released than that in the second, from which it follows that considerable hygroscopic moisture generally indicates that the rock (if igneous or metamorphic) has been severely weathered. In such cases the content of carbon dioxide is often appreciable.

Hydrogen enters into a large number of rock-forming minerals as an essential constituent. Some of the principal groups and species, roughly graded according to their average water content, are:

* S. B. Hendricks, R. A. Nelson, and L. T. Alexander. *Amer. Chem. Soc. J.*, 1940, **62**, 1457-1464.
R. E. Grim and R. A. Rowland. *Amer. Mineralogist*, 1942, **127**, 746-761; 801-818. *Amer. Ceram. Soc. J.*, 1944, **27**, 65-76.

† P. Nutting. *U.S. Geol. Survey Prof. Paper* 197-*E*, 1943.

‡ C. S. Ross and S. B. Hendricks. *U.S. Geol. Survey Prof. Paper* 205-*B*, 1945, p. 48.

		Percentage Water Content.
Zeolites :	Chabazite	21·2
	Stilbite	17·2
	Philipsite	16·5
	Heulandite	14·8
	Harmotome	14·1
	Thomsonite	13·9
	Scolecite	13·8
	Natrolite	9·5
	Analcite	8·2

Kaolinite, 14 per cent. *Meerschaum*, 12 per cent. Minerals of the kaolin group give off their water at about 950° C.*

Chlorites. Clinochlore approx. 13 per cent. Other chlorites variable.

Vermiculites. Over 10 per cent. 10 per cent. given off below 110°, the rest above 300° C.

Serpentine. 12·9 per cent.

Talc. 4·8 per cent. Half of the water is lost below dull red heat ; the rest is lost between 875° and 960° C.

Clintonites. 4·7 per cent.

Micas. Muscovite 4·5 per cent. Other micas variable with anything up to 5 per cent. Last of the water given off slowly at high temperature.

Sericite. A sericite containing 5·8 per cent. of water and an excess of soda lost most of its water at 450°-600° C.†

Clay Minerals. Illite loses hydroxyl water from 350°-600° C., changing to an anhydrous modification. *Montmorillonite* behaves likewise, but over the shorter temperature range 500°-600° C.‡

Prehnite. 4·4 per cent.

Cancrinite. 3·9 per cent.

Tourmaline. 3-4 per cent.

Amphiboles. Approximately 2 per cent. Tremolite 2·2 per cent. Water given off at about 900° C.§ The author's experience is that most hornblendes require a temperature of about 1000° C. to drive off all their water.

Epidotes. About 2 per cent. Most of the water is given off at temperatures in excess of 1,000° C.||

Staurolite. 2 per cent. Given off at very high temperature.

Topaz. Variable. Given off at very high temperature.

Chondrodite. Variable. Given off at very high temperature.

Pyroxenes. Few tenths up to 1 per cent.

Sphene. Analyses by T. G. Sahama show 0·49-1·13 per cent. of combined water removed by sodium tungstate and lead fluxes at high temperature.**

* H. Insley and R. H. Ewell, *J. of Research of the National Bureau of Standards*, 1935, **14**, 615.

† D. B. Meyer, *Amer. Min.*, 1935, **20**, 384-388.

‡ R. E. Grim and W. F. Bradley. *J. Amer. Ceram. Soc.*, 1940, **23**, 242 248.

§ E. Posnjak and N. L. Bowen, *Amer. J. Sci.*, 1931, *Ser.* 5, **22**, 203-214.

|| A. F. Smethurst, *Mineralog. Mag.*, 1935, **24**, 177.

** *Bull. Comm. Géol. Finlande.* No. 138, 1946, pp. 88-120.

Many analyses of rocks and minerals, particularly the older ones, are in error owing to an insufficient temperature being used in the water determination. Consideration of the above list, where difficulty is caused by several of the commonest mineral groups and species — *e.g.*, the epidotes, amphiboles, micas, staurolite, talc, topaz, chondrodite — shows the inadequacy of glass tubes, and in several cases of silica tubes, in a gas furnace unless the latter be unusually efficient.

Upon heating hydroxides and basic or acid salts, water is given off, usually at a red heat. The hydrogen and oxygen giving rise to this water are considered to enter intimately into the structure of the mineral, principally as hydroxyl groups, rather than to occur as water. In other minerals, usually described as hydrous — *e.g.*, the zeolites, kaolin, etc. — the water is removed at more moderate temperatures, or even by the action of desiccants in a vacuum desiccator at normal temperatures. It is customary to refer to this as water of crystallization and consider it to exist as water in the compound. Owing to the lightness of the oxygen and hydrogen atoms, X-ray studies have not afforded such definite evidence with regard to them as they have in the case of the heavier atoms.

When the elements of water are essential, their removal may destroy the mineral and give rise to one or other new minerals. In such cases a high temperature is usually required. Thus the tremolite formula $H_2Ca_2Mg_5(SiO_3)_8$ of W. T. Schaller (1916) and B. E. Warren (1931), which requires 2·22 per cent. H_2O, has recently been substantiated by E. Posnjak and N. L. Bowen.* They show that, when the water is lost at about 900° C., the material is converted into a mixture of pyroxene (diopside-clinoenstatite) and silica (which would become cristobalite if the temperature were raised to 1,200° C.). The minerals of the kaolin group give off their water at about 950° C. with a sharp, intense, exothermic effect.† At this temperature they dissociate into an intimate mixture of alumina and silica. It had

* *Am. J. Sci.*, 1931, Ser. 5, **22**, 203-214.
† Insley and Ewell, *op. cit.*

previously been shown by C. S. Ross and P. F. Kerr,* in their study of the clay minerals that, although the major portion of the water is driven off between 400° and 600° C., kaolinite and dickite require 800° C., and halloysite and nacrite a considerably higher temperature before dehydration is complete.

When the hydrogen is expelled at temperatures much in excess of 900°, it is best to decompose the mineral with a flux, when the water may be obtained at a lower temperature (see p. 93).

When a mineral contains an excess of water over the theoretical value, as is sometimes the case, it is due to surface adsorption and is given off gradually on heating. The water content of felspars, which is non-essential, is mostly driven off between 800° and 900° C.†

The discovery of heavy water containing heavy hydrogen has led to the suggestion that it may be found in the salt hydrates formed by the evaporation of ancient lakes, and in chlorites and micas.‡ E. H. and H. E. Riesenfeld have examined the water of crystallization of polyhalite and gypsum but could not find sufficient heavy water to affect the pyknometer.§ The pyknometer method, however, is by no means the most sensitive.

If, in addition to hydrogen, chlorine, fluorine, or sulphuric anhydride are present, the corresponding acids will be released and cause various troubles if a retainer is not used (see pp. 101-102). If the hydrogen is present as hydrocarbons, they will be oxidized to carbon dioxide and water.

CARBON.—In the mineral kingdom carbon occurs in the crystalline state as diamond and graphite, amorphous in many carbonaceous deposits such as coal, and as hydrocarbons in petroleum and bitumen. The carbonates of calcium, magnesium, and iron are ubiquitous, and great rock-masses are mainly composed of them. The only rock-forming silicate of importance containing carbon as an essential constituent is cancrinite, $H_6Na_6Ca(NaCO_3)_2Al_8$-

* *U.S. Geol. Survey Prof. Papers* 185 (1934) and 165 (1931).

† G. R. Skelton and H. H. Holscher, *Bureau of Standards Research Paper* 420, 1932, p. 356.

‡ V. Vernadsky, *Comp. rend.*, 1934, **199**, 694-696.

§ *Ber.*, 1934, **67** (B), 1659-1660.

$(SiO_4)_8$, which occurs in association with nepheline, but carbon dioxide often appears in analyses of scapolites and scapolitized rocks.

In igneous and metamorphic rocks carbonates are frequently present. They may be primary or introduced as the result of weathering or hydrothermal alteration, calcite and dolomite being the most widespread and abundant of secondary minerals. Graphite is much more common among m morphic than igneous rocks. It occurs in small grains and scales in some granites, syenites, and pegmatites, and has been recorded by A. Williams from peridotite and eclogite nodules in kimberlite.* In many cases there is evidence suggestive of derivation from sediments, but deoxidation of carbon dioxide released on the intrusion of igneous rocks into carbonates has also been suggested.† Among metamorphic rocks, graphite is particularly common in metamorphosed limestones, quartzites, etc. In many cases it has resulted presumably from the alteration of hydrocarbons. A summary with bibliography of the various modes of occurrence of graphite is given by Fisher (*op. cit.*). Small amounts of carbon occur in igneous rocks as carbon dioxide inclusions in quartz. Hydrocarbons occur in small amount as fine coatings or layers in many sediments and schists. Usually they are accompanied by iron oxide, with which they may be confused, particularly under the microscope. It is, however, in coals and bituminous rocks that carbon is most abundant.

Zirconium.—The silicate of zirconium, zircon, is one of the most constant accessory minerals of igneous, metamorphic, and sedimentary rocks. If thin sections, or better a concentrate of the non-magnetic portion of the heavy mineral residue of a rock has been examined, an approximate idea of the zirconia content will have been gained. Zirconia is given as 0·04 per cent. in the Clarke-Washington list. G. von Hevesy and K. Würstlin, as the result of the examination of 1,175 rock samples (X-radiographically) found the zirconium content to vary from an average of 0·03 per cent.

* "The Origin of the Diamond," London, 1932, p. 386.

† L. W. Fisher, *Amer. Min.*, 1934, **19**, 169-177.

Zr in granites to 0·006 per cent. in peridotites.* These figures are in agreement with the average content of zircon in plutonic igneous rocks where zircon rapidly becomes scarce in rocks more basic than diorites. Zirconium is also a constituent of the rare zirconosilicate minerals eudialyte, låvenite, rosenbuschite, etc. It may also enter some rock-forming silicates where its presence may not be suspected — *e.g.*, H. S. Washington and H. E. Merwin have shown that zirconia, together with the rare-earths, is present in acmite and pyroxenes with a high content of the acmite molecule.†

In igneous rocks, zirconium is generally most abundant in acid types and those rich in soda. In the latter it is sometimes concentrated, as in eudialyte-syenite and some nepheline-syenites and their pegmatites, when the zirconia content rises far above the average and may reach 2 per cent. or more. Zircon-pyroxenites occur as inclusions in kimberlite,‡ and large zircons associated with basic rock in Wisconsin have been described by Wilcox.§

FLUORINE.—Fluorine is a very widespread constituent among rocks and minerals, and few generalizations, if any, can be made with regard to rock types in which it is most prone to occur. Every specimen can be roughly assessed on petrographic examination as to the probability of appreciable fluorine by consideration of the proportion of minerals likely to contain it. Unfortunately the rock-forming silicates which usually carry fluorine vary considerably in their content of it. On the whole it is much more abundant in the acid rocks than the basic ones, but on the other hand it is sometimes enriched in highly sodic types. Rocks in the neighbourhood of acid intrusions may become considerably enriched in fluorine during pneumatolysis — *e.g.*, greisens, tourmalinized rocks, and many of the mica-hornfelses.

Fluorine is an essential constituent of fluorite CaF_2, topaz $(Al(F,OH)_2)AlSiO_4$, most apatite (fluor-apatite

* *Zeits. Anorg. Chem.*, 1934, **216**, 305-311.

† *Amer. Min.*, 1927, **12**, 233.

‡ A. Williams, "The Origin of the Diamond," London, 1932, p. 388 and plate 127.

§ *Amer. Min.*, 1936, **21**, 459.

$(CaF)Ca_4(PO_4)_3$), tourmaline, and some micas (phlogopite, zinnwaldite, and lepidolite). In many more rock-forming minerals fluorine may be interchangeable with oxygen or hydroxyl groups, but the extent of this cannot be foretold. It is for this reason, more than any other, that difficulty is experienced in forecasting the probable fluorine content of a rock or mineral. Thus fluorine is generally present in micas, amphiboles, chondrodite and other minerals of the humite group, vesuvianite, and apopohyllite. Biotite usually contains up to 2 per cent. of fluorine, phlogopite up to 5-6 per cent., but in lepidolite, zinnwaldite, and polylithionite the figure may rise to 7 per cent. or more. It has recently been shown that the sphene (titanite) lattice contains fluorine and hydroxyl in surprising amounts. Thus six analyses by T. G. Sahama* of sphenes from gabbro, limestones, and several nepheline syenites show from 0·10 to 1·40 per cent. of fluorine. A. W. Jaffe recently found fluorine (0·12-0·68 per cent.) in sphene from fifteen countries.†

On the Clarke-Washington list fluorine is given as 0·03 per cent., but there is reason to believe that this figure may be low on account of (*a*) the relative infrequency with which fluorine was determined in the older analyses and indeed in many modern ones, (*b*) the figure obtained for fluorine by gravimetric methods is usually somewhat low.

CHLORINE.—As a constituent present to the extent of only a few hundredths of one per cent., chlorine is extremely common in rocks. In the highly sodic rocks, particularly those bearing nepheline, the chlorine content rises. It is an essential constituent of sodalite, nosean, ameletite (a mineral allied to nepheline which has been reported from a number of the New Zealand phonolites), and of scapolite containing the marialite molecule ($Na_4Al_3Si_9O_{24}Cl$). Since the chlorine content of scapolites may rise to over 4 per cent., scapolitized rocks, particularly contact altered limestones, may contain a considerable amount. In the more basic rocks the apatite may be a chlorine-bearing variety.

L. S. Selivanov (*Compt. Rend.* (*Doklady*) *Acad. Sci.*

* *Bull. Comm. Géol. Finlande, No.* 138, 1946, pp. 88-120.
† *Amer. Min.*, 1947, **32**, 637-642.

U.R.S.S., 1940, **28,** 809-813) reports that, in 23 plutonic rocks of various types, the average content of chlorine is $3{\cdot}14 \times 10^{-2}$ per cent. and of bromine $1{\cdot}62 \times 10^{-4}$ per cent. In meteorites values of the same order were obtained. Dashkesanite contained 3·25 per cent. Cl, and $2{\cdot}9 \times 10^{-4}$ per cent. Br. Dashkesanite is an uncommon chlorine-bearing variety of amphibole described by G. A. Krutov (*Bull. Acad. Sci.*, U.R.S.S., *Cl. Sci. Mat. Nat.*, *Sér. Géol.*, 1936, 341-373 ; *Mineralog. Absts.*, **6,** 438) as the predominant constituent of a skarn surrounding magnetite sheets in Transcaucasia. The original analysis showed Cl 7·24, F nil, H_2O (+ 110°) 1·05 per cent. The associated igneous rocks at Dashkesan contained up to 0·13 per cent. Cl.

SULPHUR.—This ubiquitous element comes fourteenth on the Clarke-Washington list and is present in most igneous and metamorphic rocks, as well as many sediments. It occurs most commonly in the sulphide condition as pyrite and pyrrhotite, less frequently as chalcopyrite and sometimes other sulphides, and occasionally as lazurite $Na_4(NaS_3Al)Al_2(SiO_4)_3$. In the oxidized condition, sulphur is an essential constituent of haüyne and nosean, and occurs in some cancrinites and scapolites.

The sulphides are much more abundant in the basic than acid rocks, reaching their maximum development in the gabbros and norites. In mineralized districts the content of sulphides may be considerable. If the sulphur content is more than about 0·2 per cent., the sulphide mineral is usually visible in the hand specimen. In gabbro pegmatites the blebs of sulphide may be very conspicuous.

The sulphur of haüyne, nosean, lazurite, and gypsum may be leached with acid, but barytes will remain insoluble, and the sulphate of scapolites, too, will not be extracted. Moreover, if there should be soluble barium present (say as the carbonate, witherite), it will precipitate its equivalent of sulphur as barium sulphate if the acid method is used for sulphur. Care must therefore be taken in selecting the method for sulphur determination. Haüyne, nosean, and lazurite occur mostly in highly sodic rocks low in silica. The first two minerals, together with some scapolites, are unique among silicates in allowing sulphur to enter their

constitution.

Native sulphur occurs only in rocks from volcanic districts where it sometimes forms a cement to tuffs, but the analyst is unlikely to meet with it.

RARE-EARTHS.—The rare-earths, so far as is known, occur in notable amount in rocks only where there is very high soda. They also occur in allanite (the cerium epidote), monazite, and xenotime, which are not infrequently found in small amount as accessory minerals in the more acid plutonic rocks. Monazite, for instance, is a constant accessory in all the Amorican granites of Devon and Cornwall and many of those of the same age in Normandy and Britanny,* but the amount is small when the high degree of concentration employed to detect it is considered, and it is improbable that the rare-earth oxide would often exceed one or two hundredths of one per cent. Granitic and dioritic gneisses often contain monazite — *e.g.*, the Jobourg gneisses of the Cotentin.† Both monazite and xenotime are present in some of the Scottish granites.‡ In the pegmatites of syenites and nepheline syenites, considerable concentration of the rare-earth minerals may be present. In nepheline-syenites themselves rare-earth minerals such as those of the mosandrite group and rosenbuschite are sometimes present.

CHROMIUM.—Chromium is generally met with in the more basic rocks, especially those high in magnesia and low in silica. Although frequently present in very small amount, particularly in the acid rocks, its determination ought not to be neglected for the following reasons : (*a*) It adds only ten minutes to the lengthy determination of vanadium, which in most rocks is rather more abundant than chromium. (*b*) Chromium can be determined with great accuracy (to three places of decimals), so that values less than one hundredth of one per cent. have a geochemical significance.

In the most basic rocks the chromium content rises rapidly and characteristic green-coloured chromiferous varieties of common rock-forming minerals make their appearance — *viz.*, chrome-diopside, chrome-tremolite, the

* A. W. Groves, *Geol. Mag.*, 1930, **67**, 218-240.
† *Op. cit.*, pp. 226-227.
‡ *Trans. Edin. Geol. Soc.*, **13**, 85-86.

chromium mica fuchsite, uvarovite (chrome-garnet), tawmawite (chrome-epidote). Other chromium-bearing varieties are the chlorites kammererite and kochubeite. The two rock-forming minerals carrying the greatest amount of chromium are chromite and picotite (chrome-spinel).

Both chromite and picotite occur principally in igneous rocks rich in olivine and enstatite, such as the peridotites and serpentines, where they may be confused with magnetite. They also occur in the more magnesian crystalline schists. In some cases a hydrothermal origin has been suggested for chromium-bearing minerals.*

Chrome varieties of rock-forming minerals are of frequent occurrence in the deep-seated rocks such as eclogite and kimberlite. This has been further borne out by the work of G. Hevesy, A. Merkel, and K. Würstlin, who determined the chromium content of a number of rocks by X-ray spectroscopy.† The mean content in 282 intrusive rocks is Cr 0·053 per cent., in 187 extrusives 0·074, in 300 clay-shales and phyllites 0·036. In a moldavite 0·033 per cent. Cr was found, and in deep-sea red clay 0·063. The Clarke-Washington average for Cr_2O_3 is 0·05 per cent.

VANADIUM.—Vanadium is very widely distributed in rocks of all kinds, igneous, metamorphic, and sedimentary.‡ It is found in such varied sediments as coals, clays, limestones and sandstones, and vanadium-rich nodules have been described from the New Red Sandstones of Budleigh Salterton, Devon, by G. E. L. Carter (*Mineralog. Mag.*, 1931, **22,** 609-613). Hillebrand has shown that vanadium occurs in the more basic igneous and metamorphic rocks up to 0·08 per cent. or more of V_2O_3, but it seems to be absent or nearly so from the highly siliceous rocks. Some of their ferric aluminous silicate constituents carry still higher percentages—up to 0·13 per cent. V_2O_3 in a biotite separated from a pyroxene gneiss.§

* P. Eskola, *Comp. rend. Soc. Geol. Finlande*, 1933, No. 7, pp. 26-44.

† *Z. anorg. Chem.*, 1934, **219,** 192-196.

‡ Hevesy, Alexander and Würstlin, *Zeit. f. anorg. Chem.*, 1930, **194,** 318.

§ Hillebrand-Lundell, "Applied Inorganic Analysis," New York, 1929, p. 352. The present author does not agree with Washington that Hillebrand laid undue stress on the importance of the vanadium content of igneous rocks (Washington, p. 19).

Among rock-forming minerals, it enters as a minor constituent of ferric aluminous silicates such as biotites, amphiboles, and pyroxenes. Since it appears to replace the sesquioxides in these minerals it is usually returned in analyses as V_2O_3 and not as V_2O_5. Vanadium also occurs in ilmenite associated with titanium-rich minerals. Thus the pyroxenite ores of the Azhinsk gabbro complex of Oirotia, Western Siberia (TiO_2 4 per cent. and V_2O_5 0·1 per cent.) contain 42 per cent. of titaniferous augite. The associated ilmenite-gabbro contains approximately TiO_2 5 per cent., V_2O_5 0·1 per cent. Separation of the minerals from this ilmenite-gabbro gives a titaniferous augite with 9 per cent. TiO_2, and a magnetic fraction containing 21 per cent. TiO_2 and 0·42 per cent. V_2O_5, showing that vanadium enters almost wholly into the ilmenite molecule.* Large deposits of vanadium-bearing magnetite-ilmenite, associated with bodies of gabbro in the anorthosite core of the Adirondack Mountains, have been reported from near Lake Sanford, Essex Co., New York.† The district as a whole contains 16,500,000 tons of measured ore (not to mention large tonnages of indicated and inferred ore), which will yield 10,000,000 tons of magnetic concentrates with an average content of 0·6 per cent. V_2O_5. The magnetic concentrate from the ore may contain up to 15 per cent. TiO_2, incorporated in ilmenite and rutile, and up to 1.7 per cent. V_2O_5, possibly in very fine-grained coulsonite, an iron-vanadium oxide, which is included in the magnetite. Vanadium has been reported recently as being widespread in manganese ores from the south-western United States.‡

For the distribution of vanadium in iron ores, and in the irons and slags resulting from them see T. Deans, *Bull. Imp. Inst.*, 1948, **46,** 104-110, and A. Kvalheim, *Norsk. Geol. Tidsskrift*, 1942, **21,** 245-267.

Vanadium also enters many ores in minute amounts, and it has been suggested that the vanadium in certain oxidized ores has been derived mainly from the primary vein minerals, and possibly to some extent from the igneous and sedimentary

* P. I. Lebedev and A. P. Lebedev, *Comp. rend. Acad. Sci. U.R.S.S.*, 1934, **3,** 294-300.

† J. R. Balsley. *U.S. Geol. Survey Bull.*, 940-D, 1943.

‡ *Economic Geology*, 1945, **40,** 82-83.

rocks surrounding the deposits.* A. C. Skerl suggests that the vanadium minerals of Broken Hill, Northern Rhodesia, were derived from the surrounding sedimentary rocks.† V. Lebedeff and G. Chonbert have shown that the rocks surrounding the mineral deposits of the Niari basin, French Equatorial Africa, are strongly impregnated with vanadium.‡

The amounts of vanadium present in sedimentary rocks have been studied by K. Jost, who also made a large number of new determinations. His averages are clays and shales 0·012 per cent. V, sandstones 0·002 V, and still less in limestones and dolomites. Residual deposits, such as laterites and bauxites, as well as sedimentary iron ores and manganese ores, and rocks containing organic remains, bitumen, or coal, give higher figures. His average for igneous rocks is 0·018 V, and on weathering he considers that this goes mostly into the clays when, in the presence of organic matter, there is further enrichment from solution, due to reduction, especially in arid climates.§

This may have some bearing on the formation of the highly vanadiferous nodules of Budleigh Salterton, for the vanadium may have been largely derived from the Dartmoor granite or its vein rocks and apophyses|| at a period when the climatic conditions were certainly arid.

Vanadium is transported to the ocean and there precipitated along with the oxides of iron and aluminium in the red clays and terrigenous marls of the sea bed. Biochemical reactions are believed to play an important part in the deposition of vanadium in these deposits. It is known to occur in sea-water in the bodies of holothurians and other animals** which accumulate after death in the ocean bottom deposits. That vanadium enters into vegetable and some animal life is also indicated by its presence, often in considerable amounts, in the ashes of coals, bitumen, asphalts, and petroleum.††

* W. H. Newhouse, *Amer. Min.*, 1934, **19**, 209-220; G. E. Clausen, *ibid.*, pp. 221-224.

† *Min. Mag.*, London, 1934, **50**, 280-283.

‡ *Compt. rend. Acad. Sci. Paris*, 1934, **198**, 484-486.

§ *Chemie der Eerde*, 1932, **7**, 177-290.

|| A. W. Groves, *Q.J.G.S.*, 1931, **87**, 66-70.

†† W. Lindgren, "Mineral Deposits," 3rd ed., pp. 460-461.

** *Ibid.*, pp. 32 and 285.

In this connection it is of interest to note that the extraction of vanadium from soot derived from the burning of oil from the Lake Maracaibo region of Venezuela has been carried out as a commercial process. In an article on analyses of petroleum-coke, R. C. Wells* records the presence of 0·22 per cent. V_2O_5 in tar in breccia from Terlingua, Texas; 0·043 per cent. V_2O_5 (equivalent to 61 per cent. of the ash) in asphalt from Baboso well I, Bermudez Lake, Venezuela; 12·2 per cent. in ash from grahamite from near Page, Oklahoma; and 45 per cent. in the ash of asphalt from Nevada. Of the 24 analyses of U.S.A. petroleum-coke ashes presented, the V_2O_5 content varied from nil to 6·2 per cent. (See also the introductory section to this Chapter, pp. 260-261.)

NICKEL.—Nickel occurs principally in the more basic rocks where it is located in the ferromagnesian minerals, particularly olivine, serpentine, micas, chlorites, and amphiboles. It also occurs in pyrite and pyrrhotite, the latter frequently carrying nickel in the gabbros. Olivine or biotite carrying nickel will pass it on to their decomposition products, serpentine and chlorite respectively. It is very noticeable that nickel is usually associated with high magnesia. Nickel-iron alloys are typical of the meteoric irons and some rare cases have been reported from basalts.

R. C. Wells† has made new determinations of nickel on 150 rocks of all kinds previously analysed by the U.S. Geological Survey, using the modern method of Sandell and Perlich (see p. 187), which compares very well with the spectrographic method. His results bear out the previous paragraph (written in 1936) in every way. In general the percentage of nickel increases with the density of the rocks. In silicate rocks nickel predominates in the ferro-magnesian varieties, being definitely allied to rocks with high magnesia content and with density greater than 2·85. The content is markedly high in dunite, peridotite, and other rocks containing olivine, and, of course, is still higher in olivine separated from them. Nickel is also present in sea water, and in some peat and petroleum.

* Contributions to Geochemistry, 1942-45. *U.S. Geological Survey Bulletin* 950, Washington, 1946, pp. 3-5.

† *U.S. Geol. Surv. Prof. Paper* 250-A, 1943.

Wells found the average of all his new determinations of nickel in igneous rocks to be about 0·008 per cent. He estimated 0·016 per cent. to be a reasonable figure for the relative abundance of nickel in the whole of the 10 mile crust.

The amounts of NiO most commonly met with in rocks range from 0·01 per cent. or less to 0·10 per cent. or more in highly magnesian rocks and ferromagnesian minerals separated from them. Higher values will seldom be encountered, except in kimberlites and in olivines separated from nickel bearing rocks. Many of the determinations made before the introduction of dimethylglyoxime tend to be high. In spite of the small amounts present in rocks, the gravimetric dimethylglyoxime method as applied by H. F. Harwood and L. S. Theobald* enables accuracy to two places of decimals to be uniformily maintained, and 0·01 per cent. NiO can be determined on a 2 g. sample. The method of Sandell and Perlich,† given on p. 187, takes much less time to carry out and makes it possible to determine nickel to ten-thousandths of one per cent. with a gram or less of material. It is thus particularly suitable for the determination of nickel in acid rocks or whenever the content is very low, but requires modification where the proportion of Ni exceeds about 0·07 per cent.

Cobalt.—So far as is known, cobalt usually accompanies nickel in rocks though it is almost invariably present in smaller amount. The small amounts of cobalt present in rocks may be determined together with nickel if desired, by the method of Sandell and Perlich (*Ind. Eng. Chem. Anal. Ed.*, 1939, 309 and 364). Cobalt is an important constituent of meteoric irons.

That cobalt may sometimes be introduced into rocks by hydrothermal agencies is indicated by the description of a cobaltiferous staurolite—lusakite—from Northern Rhodesia,‡ where it occurs as a quartz-magnetite-lusakite rock.

Barium and Strontium.—Barium is an extremely widespread element occurring in most rocks, igneous, meta-

* *Analyst*, 1933, **58**, 673-682.
† *Ind. Eng. Chem.*, *Anal. Ed.*, 1939, **11**, 309-311.
‡ A. C. Skerl and F. A. Bannister, *Min. Mag.*, 1934, **23**, 598-606.

morphic, and sedimentary. The sulphate, barytes, may be present, particularly in the sediments, and sometimes witherite, but in igneous rocks barium is more often located among the silicates. It occurs as hyalophane $(K_2Ba)Al_2(SiO_3)_4$ associated with orthoclase, and less commonly as celsian $BaAl_2Si_2O_8$ associated with the lime-soda felspars or with orthoclase. Sometimes it occurs in micas, a barium variety of muscovite being known as œllacherite. For calculations indicating the mineralogical location of barium in rocks, see the author's paper on the charnockite series of Uganda.* Since the most common mode of occurrence in igneous rocks is as hyalophane or celsian associated with orthoclase, it follows that barium is typical of potassic rocks. Some zeolites carry barium. In the great majority of igneous rocks BaO varies from nil to 0·25 per cent. Figures in excess of 0·5 per cent. are uncommon except in sediments where 1 per cent. or more may be present. W. Noll has recently shown that the average amount of BaO in igneous rocks is about 0·05 per cent., with a decided preference for granitic rocks.† It is a fact, however, that barium is very abundant in certain biotite-pyroxenites as well as in leucitic rocks. In the author's own experience six analyses of mica averaged 0·18 per cent. BaO with a maximum of 0·23 per cent. W. von Engelhardt‡ finds BaO in igneous rocks ranges from 0·2 per cent. in syenite to 0·0003 in peridotite, with an average of 0·048. In sedimentary rocks it is adsorbed by clay, clay-slates containing BaO 0·05 per cent. and limestone 0·01. The average for the whole lithosphere is 0·045 per cent. Rocks containing the higher oxides of manganese may contain appreciable barium in psilomelane or hollandite.

It has been long recognized that barium, like strontium, has a decided tendency to characterize the rocks of particular regions. One of the first of these to be demonstrated was the area east of the Rocky Mountains, from Colorado to Montana, which is particularly rich in both elements. Barium and strontium frequently occur in the rocks of the

* *Q.J.G.S.*, 1935, **91**, 175-176.
† *Chemie der Erde*, 1934, **8**, 507-600.
‡ *Chemie der Erde*, 1936, **10**, 187-246.

backbone of Africa from Egypt to South Africa. In Uganda they occur in the rocks of the Basement Complex, including the charnockite series, where barium preponderates.* At the opposite end of the geological column, the lavas (Tertiary to Recent) of Uganda carry appreciable amounts of both baria and strontia.† A specimen of olivine-melilitite collected by the author at the Katwe crater and analysed by H. F. Harwood contained 0·24 per cent. SrO; other volcanics from this locality contain about 0·15 per cent. SrO.‡ In Southern Rhodesia SrO is frequently more abundant than BaO, according to the published analyses of the Geological Survey of that country.§

According to P. Eskola, BaO is mainly associated with the potash minerals and SrO with lime minerals.‖ Noll (*op. cit.*), who has made many additional determinations of both oxides, maintains that SrO has a preference for alkali rocks, BaO occurring more in granites. Holmes (*op. cit.*, 1932, p. 423) shows that world averages for the chief families of igneous rocks show a tendency for both BaO and SrO to vary with the product of CaO and K_2O. His table of figures shows that SrO is highest in rocks rich in leucite and melilite but lower in the nephelinites and phonolites. Similarly, the leucitic rocks of Java, frequently show more SrO than BaO.** On the other hand, the high content of BaO and SrO exhibited by some microdiorites and other dyke rocks may have been enriched by hydrothermal activity.

The mineralogical location of strontium is still doubtful and will be settled only by the isolation and analysis of minerals in strontia-rich rocks, but it is significant that in five analyses of muscovite, biotite, and phlogopite made by the author SrO averaged 0·03 per cent. and reached a maximum of 0·07 per cent. Similarly, two analyses of hornblende gave 0·03 per cent. and 0·07 per cent. SrO. Noll (*op. cit.*) gives the average for SrO in igneous rocks as about 0·05 per cent.

* A. W. Groves, *op. cit.*

† A. Holmes and H. F. Harwood, *Q.J.G.S.*, **88**, 1932, 420.

‡ A. Holmes and H. F. Harwood: *Uganda Geol. Survey, Memoir III*, Part II, 1936, § 768, Analyses V and W.

§ "Chemical Analyses of the Rocks, Ores and Minerals of Southern Rhodesia," by E. Golding, *Geol. Survey Bull.*, No. 29, 1936.

‖ *Amer. J. Sci.*, Ser. 5, **4**, 331-375.

** *J. Geol.*, **22**, 231-245.

He states that in the minerals of sedimentary rocks strontium is associated with calcium, but more in aragonite and anhydrite than in calcite, gypsum, and dolomite. E. R. Trueman* has called attention to the fact that molluscan shells usually contain traces of strontium when they consist of aragonite, but not apparently when the shells consist of calcite. The results of G. von Hevesy and K. Würstlin,† measured X-radiographically on 1,046 samples — *viz.*, average of volcanic rocks 0·011 per cent. Sr and 0·002 per cent. for sedimentary rocks — are lower than those obtained by chemical analysis. A strontium-anorthite has been prepared artifically but is not known to occur in rocks.‡

As a result of the slow β decay of rubidium into a stable isotope of strontium, small quantities of radiogenic strontium have accumulated in minerals containing rubidium. L. H. Ahrens has calculated§ that about 0·5-1·0 per cent. of the total strontium in the earth's crust must be radiogenic. He finds the minerals richest in radiogenic strontium to be lepidolite, amazonite, hydrothermal microcline other than amazonite, pollucite, and some specimens of muscovite and biotite, particularly those which tend to be enriched in lithia. In general, rocks rarely seem to contain a high proportion of radiogenic strontium, although some ancient granite and gneissic types from Finland have from 15 to 30 per cent. of their strontium in radiogenic form. A further outcome of Ahren's work is the evident need in discussions on the Ca-Sr-Ba association in minerals and rocks, to take into account the approximate age and rubidium content.

BERYLLIUM.—Beryllium has very rarely been returned in the analyses of igneous rocks, though there are one or two instances among the analyses made by the Geological Survey of Great Britain.|| Yet, as Clarke and Washington have

* *Nature*, 1949, **153**, 142.

† Z. *anorg. Chem.*, 1934, **216**, 312-314.

‡ E. Dittler and H. Lasch, *Anzeiger Akad. Wiss. Wien*, Math.-naturwiss, Kl., Abt. I., 1930, 201-203; *Sitzungsber. Akad. Wiss. Wien*, Math.-naturwiss. Kl., Abt. I., 1931, **140**, 633-674.

§ *Mineralog. Mag.*, 1948, **28**, 279.

|| "Chemical Analyses of Igenous Rocks, Metamorphic Rocks and Minerals," E. M. Guppy and H. H. Thomas, *Geological Survey of Gt. Britain*, 1931.

observed, the fact that beryl is not a rare mineral indicates that beryllium is fairly widespread. If it is not determined, it will be included in the figure returned for aluminia, which is an additional reason for seeking and determining it. Unfortunately, unless an ultra-violet lamp is available, there is no simple qualitative test for revealing much less than one per cent. of BeO in a rock (see p. 247). BeO should be determined in rocks, especially in pegmatites, containing or in the neighbourhood of occurrences of beryl, phenakite, chrysoberyl, and beryllonite; in recent years numerous occurrences have been reported of helvite, a beryllium mineral with similarities to the garnet group. In addition, beryllium enters into a number of rare minerals associated with nepheline-syenites and their pegmatites. Palache and Bauer have shown that alumina has been mistaken for beryllia in vesuvianite,* but this was contradicted by Silbermintz and Roschkova,† who, however, relied on the quinalizarin test. The occurrence at Franklin, New Jersey, of a beryllium vesuvianite in which 9·20 per cent. BeO replaces alumina has been described by C. Palache.‡ The beryllium in this instance is considered to be a post-ore element introduced into the deposit from intrusive pegmatite.

V. M. Goldschmidt and Cl. Peters,§ in a survey of the geochemistry of beryllium, point out that whereas the average content in granites may amount to 0·001 per cent. BeO, in nepheline-syenites it is 0·01. Beryllium tends to be concentrated in residual magma, as in pegmatites, but does not occur in olivine or olivine rocks on account of the fact that it does not replace magnesium in crystals. It enters alkali felspar, nepheline, pyroxene, amphibole, and micas; probably it replaces silica in complex silicic acids. In the sedimentary rocks they find that beryllium tends to occur with high aluminium as in clay-slates, bauxite, and the ashes of many coals. It is not concentrated in the ores of iron or manganese. Beryllium is markedly concentrated in the contact metamorphosed products of sediments rich

* *Amer. Mineralog.*, 1930, **15**, 30.
† *Centr. Min.*, Abt. A, 1933, 249-253.
‡ *Geol. Survey Prof. Paper* 180, 1935, pp. 94-95.
§ *Nachr. Gesell. Wiss. Göttingen*, Math.-Physik Kl., 1932, 360-376.

in lime by a process which the authors believe to be metasomatic pneumatolysis. They found that beryllium goes into vesuvianite to a greater extent than into grossular, and that numerous occurrences of vesuvianite contain a relatively high amount.

COPPER.—Copper is undoubtedly present in a great many rocks in small amount (a few hundredths of 1 per cent. CuO), but in basic rocks it may rise to 0·1 per cent. CuO or more, and this in regions which are not usually regarded as mineralized; in mineralized districts higher values may be met. In the past, copper has been determined but rarely in rocks, the principal difficulty being that, unless the content of the metal was appreciable and comparatively obvious, a large sample was required in order to attain accuracy. Even so it is probable that results for copper have frequently been high owing to co-precipitation of platinum (derived from the vessels) as sulphide. Now that one of the most delicate colorimetric methods for copper has been adapted to rock analysis* such small amounts as 0·001-0·25 per cent. CuO can be determined with considerable accuracy.

The occurrence of copper as sulphides (chalcopyrite $Cu_2S.Fe_2S_3$, chalcocite Cu_2S, and in small amount in pyrite FeS_2) in rocks is well known, but the fact that it often enters amphiboles, pyroxenes, epidotes, etc., is not so generally appreciated. In a hornblende separated from an amphibolite, the author found 0·10 per cent. CuO. Short of isolating and analyzing the component minerals, it is difficult to ascertain the mineralogical location of copper in a rock when sulphur is also present. Usually it is not possible even to say whether the copper is present as sulphide or silicate, for as much as 0·04 per cent. of metallic copper requires only 0·01 per cent. of sulphur to form chalcocite or 0·02 per cent. for chalcopyrite. Since the method for the determination of copper is much more accurate than those for sulphur, it is inadvisable to conclude that, because sulphur appears to be absent or is not present in sufficient amount, the copper is located in a silicate mineral unless the excess of copper would require at least several hundredths of one per cent. or more.

* A. W. Groves, *Mineralog. Mag.*, 1935, **24**, 35-41.

Copper is also a constituent of meteorites.

LITHIUM.—Although lithium is of widespread occurrence in rocks, as shown by the spectroscope, it is rarely present in determinable amount. Except when a rock contains a lithium mineral, quantitative determinations are usually confined to analyses of the micas (particularly lepidolite, zinnwaldite, and muscovite, though biotites sometimes carry a little), beryl, tourmaline, alkali felspars, and the lithium minerals spodumene, petalite, triphylite, and amblygonite (fluo-phosphate). The last four species, together with lepidolite, are typical of granite pegmatites. Lithium is most abundant in the highly alkaline rocks, and according to Washington,* there is good reason to believe that it is especially prone to occur in those that are sodic rather than potassic. The mean lithium content of the earth's crust has been assessed at 4×10^{-5} per cent. (F. Hermann).†

The rock types likely to carry appreciable amounts of lithium are indicated by the following results of V. M. Goldschmidt, H. Berman, H. Hauptmann, and Cl. Peters :‡

Average of 24 greisens from the Erzgebirge	0·3	per cent. Li_2O	(and 0·20 Rb_2O)
Average of 14 granites	0·03	,, ,, ,,	(0·06)
Average of 22 nepheline-syenites	0·003	,, ,, ,,	(0·01)
Average of 36 schists	0·01	,, ,, ,,	(0·04)
Average of 11 gabbros	0·003	,, ,, ,,	(0·002)

The distribution of lithium in over a hundred specimens of felspar and mica, all from Southern Africa, has been investigated spectrographically by L. H. Ahrens and W. R. Liebenberg.§ Almost without exception, all the micas contained lithium, sometimes in appreciable quantity. In contrast, the presence of more than 0·0005-0·001 per cent. Li_2O was exceptional in the felspars. The only micas that did not contain lithium were some samples of phlogopite and vermiculite of metamorphic origin. The investigation showed that lithium is enriched in muscovites of later crystallization, and that, where mica and felspar are associated, lithium is always enriched in the former. There are lithium muscovites as well as lepidolites.

* "The Chemical Analysis of Rocks," New York, 1930, p. 21.
† *Metalbörse*, 1934, **24**, 535; *Chem. Zentr.*, 1934, ii, 1433.
‡ *Nach. Gesell. Wiss. Göttingen*, Math.-Physik Kl., 1933, 235-244.
§ *Trans. Geol. Soc. S. Africa*, 1945, **48**, 75-82.

Lithium is also a constituent of certain spring waters, and, in cases where such waters have flowed into a basin in a region of high evaporation, lithium has been concentrated together with the more usual salts. Thus the brine of Searles Lake in the Mohave Desert of California carries 0·032 per cent. LiCl, and this has now become one of the world's principal commercial sources of lithium. Likewise sediments associated with such basins or former basins may also carry substantial lithium values. For example, at Hector, California, a clay in an old playa carried 0·60 to 1·12 per cent. Li_2O, and clays from other old playas in California and Arizona have a comparable lithia content. An impure magnesite in the Muddy Mountains of south-west Nevada carried from 0·17 to as much as 1·77 per cent. Li_2O.*

Boron.—Until a few years ago little more was known about the distribution of boron in rocks than about that of the principal rock-forming minerals of which it is an essential constituent — *viz.*, tourmaline, datolite, and dumortierite. The position in 1929 was summarized by Hillebrand and Lundell as follows :† " No doubt boron occurs occasionally in rocks in amounts superior to some of the other constituents that are habitually determined. But the lack of accuracy of the methods that are at all applicable to mineral substances not directly soluble in acids, other than hydrofluoric acid, is accountable for the fact that no one has ever sought to apply these methods to rocks, unless boron was supposed to be present in appreciable amount." Similarly, prior to the introduction of the special flame test (see p. 239), qualitative tests have been difficult to apply.

The position has been entirely changed by the spectrographic work of V. M. Goldschmidt and Cl. Peters, who have determined the boron content of a large number of rocks and minerals.‡ The following averages are extracted from their results :

Average of 14 granites	0·001 per cent. B_2O_3
Average of 11 grabbos	0·001 ,, ,, ,,
Average of 22 nepheline-syenites	0·001 ,, ,, ,,

* *U.S. Bur. Mines Infornatiom Circular* 7054. Lithium.

† " Applied Inorganic Analysis," New York, 1929, p. 607.

‡ *Nach. Gesell. Wiss. Göttingen,* Math.-Physik Kl., 1932, 402-407, 528-545.

Average of 36 schists	0·1	,,	,,	,,
Dictyonema slate, Norway	0·1	,,	,,	,,
Ash of hard coal, Hartley, near Newcastle-upon-Tyne	1·0	,,	,,	,,

It is interesting to observe that these results indicate a much higher content of boron in sediments and altered sediments than in plutonic rocks. Likewise a number of sedimentary iron ores and the glauconitic sandstones contain 0·05 per cent., whereas the content of the igneous iron ores examined was extremely small.

The surprising discovery has been made that boron is a constant constituent of braunite in the manganese ores of the Postmasburg field in South Africa, yet peculiarly enough the other manganese minerals in these ores carry virtually no boron.* The Postmasburg ores as mined may contain 0·2 to 0·5 per cent. B_2O_3 or even more.

Platinum.—Platinum will be encountered only in the most basic plutonic rocks such as serpentines, peridotites, norites, and gabbros. It is present in some meteorites. If platinum is present in the metallic state, it will remain unattacked by the hydrofluoric and sulphuric acids in the determination of total iron, and, when the residue is fused with sodium carbonate and dissolved in dilute sulphuric acid, platinum will appear as a residue. Unattacked ilmenite or tourmaline, due to insufficient fusion, must not be confused with the metals of the platinum group. The most ready means of confirmation is to examine the non-magnetic heavy mineral concentrate by reflected light under the microscope.

Tin.—Cassiterite (SnO_2) may sometimes occur in acid granites, killas, greisens, or pegmatites where it has usually been introduced by pneumatolysis. Cassiterite may be detected in the non-magnetic heavy mineral concentrate even when the ordinary qualitative tests fail to reveal it.

Zinc.—Zinc is probably present in many rocks in small amount but very little of it would be caught even in a well-conducted analysis. A method for the determination of zinc in rocks has been devised by Sandell (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 464).

* B. Wasserstein. *Economic Geology*, 1943, **38**, 389-398.

MOLYBDENUM.—Molybdenum, as molybdenite, occurs mostly in granites, syenites, and their pegmatites but it has also been reported from gneiss and crystalline limestone.

V. L. Bosazza has shown that South African clays of Karroo age commonly contain an appreciable amount of molybdenum. A sample of such clay when heated at 1,000° C. and extracted with hot water gave 0·08 per cent. MoO_2.

Sandell has devised a method for the determination of molybdenum in rocks (see p. 246). He uses an aliquot part of the leachings from the sodium carbonate fusion for vanadium and chromium, the method being based on extraction of molybdenum thiocyanate by ether.

RUBIDIUM, CAESIUM, AND THALLIUM.—For the rubidium content of rocks see the results of V. M. Goldschmidt (and others) under Lithium (p. 290). Rubidium, like thallium, is confined essentially to potassium-rich minerals. Of these, lepidolites are richest in both rubidium and thallium with mean values of 1·5 per cent. Rb_2O and 0·015 per cent. Tl_2O.* Ahrens shows that rubidium and thallium are very closely associated geochemically, and that it is possible that this relationship between these two elements is closer than that of any other pair of elements. He finds that (*a*) the Rb_2O/Tl_2O ratio is constant for all micas and is constant for all felspars, though the ratio for the micas is not the same as that for the felspars ; (*b*) those micas associated with albite are usually richer in rubidium and thallium than those associated with microcline ; (*c*) the rubidium contents of microcline and associated muscovite are approximately the same ; (*d*) neither rubidium nor thallium could be detected in any of the five albites examined.

Microcline-perthite with up to 3·30 per cent. Rb_2O and 0·1-0·7 per cent. Cs_2O has been reported from Varuträsk, Sweden.† N. P. Kapustin‡ has shown that the intensity of the green colour of amazonite (a variety of microcline) is more or less proportional to the amount of rubidium

* L. H. Ahrens, *Trans. Geol. Soc. S. Africa*, 1946, **48,** 207-231.
† O. J. Adamson, *Geol. För. Förh. Stockholm*, 1942, **64,** 19-54.
‡ *Bull. Acad. Sci. U.R.S.S.*, Sér. Géol., 1939, No. 3, pp. 111-115.

present. Amazonite from various localities examined by him contained 0·17-1·89 per cent. Rb_2O and 0·003-0·020 per cent. Cs_2O. Microcline-perthite from a lithium pegmatite on Kluntarna Island, 75 km. N.W. of Varuträsk, contained 1·85 per cent. Rb_2O.*

R. E. Stevens and W. T. Schaller made determinations of Li, Na, K, Rb, and Cs on 43 samples of various kinds of mica, mostly from pegmatites. Lepidolite contained the largest amounts of the rare alkalis, 17 samples averaging Li_2O 4·90, Rb_2O 1·35, Cs_2O 0·24 per cent. Six biotites averaged Li_2O 0·71, Rb_2O 0·59, Cs_2O 0·30 per cent. 12 muscovites averaged Li_2O 0·26, Rb_2O, Cs_2O 0·06 per cent.

Thallium can be concentrated by ether extraction of $TlCl_3$, or by chloroform extraction of the dithizone complex, and its determination on these lines should be possible (Sandell, "Colorimetric Determination of Traces of Metals," New York, 1944, p. 411). Rubidium and caesium are collected with potassium perchlorate, or more efficiently with potassium chloroplatinate, and can be checked and approximately determined spectroscopically.

COLUMBIUM AND TANTALUM.—The commercial ores of these metals are columbite and tantalite, associates of tin and tungsten, and of wide occurrence in pegmatites. In addition there is an extensive list of minerals containing these elements as essential constituents, often with titanium. Largely owing to the analytical difficulties involved, comparatively little is known as yet regarding their occurrence in rocks and rock-forming minerals. Koppite has been reported from various limestones as a minor rock-forming mineral. Of particular interest to the rock analyst, however, is the discovery of from 0·03 to 1·10 per cent. of Cb_2O_5 in sphene from various rocks, the higher values being found in sphene from nepheline syenite.† From 0·1-1·0 per cent. Cb_2O_5 has also been reported from several sphenes out of a total of 15 examined.‡

GERMANIUM.—The principal mineral of which germanium is an essential constituent is germanite — (Cu, Ge, Fe, Zn,

* E. Grip. *Géol. För. Förh. Stockholm*, 1941, **62**, (for 1940), 380-390.
† T. G. Sahama. *Bull. Comm. Géol. Finlande*, No. 138, pp. 88-120.
‡ H. W. Jaffe. *Amer. Min.*, 1947, **32**, 637-642.

Ga)(S, As). This mineral, which contains from 5·10 to 10·19 per cent. germanium, is known only from Tsumeb, in South-West Africa. Germanium is also an essential constituent of the argyrodite ($Ag_8 GeS_6$) — canfieldite ($Ag_8 SnS_6$) series, but no concentration of these minerals constituting a commercial source of the element has yet been found. Germanium has also been reported from numerous zinc blendes, calamine, enargite, cassiterite and other tin minerals, franckeite, euxenite, and in tantalum and columbium minerals. Papish* has noted the presence of minute quantities of germanium in silicate minerals from pegmatites and high-temperature vein deposits in many parts of the world.

The work of V. M. Goldschmidt, of the Fuel Research Board, and of Morgan and Davies, on germanium in British coals, particularly from the Northumberland area, and ash and dust derived therefrom is well known and has led to the commercial extraction of the metal from such sources. Germanium has since been found in many other coals. V. M. Ratynsky†, who has studied the accumulation of germanium in 500 Russian coals, found only a low content in coals from the Urals, while those from the Caucasus contain up to 1 per cent. Ge in the ash. He concluded that ash-poor coals with much clarain-vitrain are the richest in germanium

The determination of germanium is based on the ready volatility of $GeCl_4$. A method for the estimation of germanium in rocks is described by Hybbinette and Sandell (*Ind. Eng. Chem., Anal. Ed.*, 1942, **14,** 715) ; amounts from 0·0002 to 0·0058 per cent. Ge were found in granite.

GALLIUM.—Among minerals, the germanite of the Tsumeb Mine, has the highest gallium content (up to 0·75 per cent.). Various investigators have discovered gallium — usually spectroscopically — in zinc blende ; in iron minerals, particularly magnetite and pyrites, as well as in metallic iron and meteoric iron ; in bauxite, china clays, and commercial aluminium, and in manganese ores ; in germanite and in certain mineral waters; and sometimes in beryl. In 1933, Goldschmidt and Peters discovered gallium (together

* *Econ. Geol.*, **24,** 1929, 470-480.
† *Compt. Rend. Acad. Sci. U.R.S.S.*, 1943, **40,** 198-200.

with germanium) in the ash of certain Northumbrian coals. It has also been found in the flue dusts derived from a number of Australian coals (*Trans. Roy. Soc. S. Australia*, **62,** 1938, 318-319). The occurrence of gallium has been most fully dealt with by E. Einecke, "Das Gallium," Leopold Voss, Leipzig, 1937 (155 pages).

In spite of the widespread occurrence of gallium in coals, its commercial extraction from bauxite (containing about 1 oz. of gallium to the ton) has been commenced by the Aluminium Co. of America. L. H. Ahrens* found gallium, by spectroscopic methods, in 32 out of 34 clays, from various parts of the world.

Olavi Erämetsä (*Ann. Acad. Sci. Fennicae* A54, No. 9, 5-25 (1940)) examined 226 non-metallic Finnish minerals and found gallium widely distributed in them. He found gallium to be concentrated in the weathering products of cordierite; and beryllium-rich minerals, such as chrysoberyl, to be also gallium-rich. Of the aluminous minerals, the felspars and micas were rich in gallium, which accounts for the gallium content of granites; there appeared also to be some relation between the gallium and aluminium content of minerals.

A method for the determination of gallium in silicate rocks has been given by E. B. Sandell, *Anal. Chemistry*, **19,** 1947, 63-65.

URANIUM.—The uranium content of the earth's crust has been estimated by various authorities at 0·0002 to 0·0009 per cent. Over fifty mineral species containing uranium are known but most of these are rare. The outstanding primary mineral is pitchblende, and its crystal variety uraninite, which are essentially uranates of uranyl and lead. Also of primary occurrence are the group of complex columbium-tantalum-titanium minerals, which often contain considerable amounts of uranium. In addition, there are several rare-earth phosphates, such as monazite and xenotime, and silicates, such as allanite, tscheffkinite, zircon (cyrtolite), and gadolinite, that not infrequently contain uranium. The primary uranium minerals are prone to alteration and break down under weathering

* *S. African J. Sci.*, 1945, **41,** 152-160.

agencies giving rise to numerous secondary minerals among which green, yellow, and orange colours are often prominent. Pitchblende is characteristically a vein-forming mineral, and is usually associated with cobalt, nickel, silver, and copper. The other primary uranium minerals, including uraninite, are practically confined to the granitic pegmatites, and it is generally recognized that the association of uranium-bearing minerals with potash-felspar-rich pegmatites is well marked.* In view of the fact that the secondary uranium minerals have originated by the precipitation of uranium salts derived from primary minerals and carried in solution by surface or circulating waters, they may occur in a great variety of rocks. Usually they have been deposited on cracks, joints, or solution channels.

Uranium also shows marked association with carbonaceous matter. As a primary occurrence there is the coal-like hydrocarbon mineral thucholite or anthraxolite which sometimes occurs in pegmatites and usually contains a considerable amount of uranium. The association with carbon is, however, much more marked in the case of secondary uranium minerals. If the element is carried in solution by surface waters into basins or other favourable catchment areas, uranium salts may be deposited as concentrations of secondary minerals. In such event, carbonaceous matter in the form of decaying vegetation or oil (but excluding carbonates) is particularly favourable to deposition, as in the case of the carnotite occurrences in Colorado and Utah, the uraniferous peaty muds of Madagascar, and the lignitic 'kolm' of Sweden. The last mentioned contains up to 0·5 per cent. uranium.

There is also a well recognised category of carbonaceous marine sediments with which a low content of uranium is associated.† Many marine sedimentary black shale and phosphorite formations contain 0·01 to 0·02 per cent. uranium. They are usually rich in organic matter and sulphides, and contain little or no carbonate. The nature of the uranium-bearing mineral or compound is not known. In contrast, non-marine black shales, as a group, are not

* L. R. Page. *Economic Geology*, 1950, **45,** 12-34.

† V. E. McKelvey and J. M. Nelson. *Economic Geology*, 1950, **45,** 35-53.

uraniferous. The phosphatic nodules found in many marine black shales are also usually uraniferous.

Many granites and related rocks contain about 0.003 per cent. uranium or thorium oxide. Contents of up to 0·01 per cent. occur more rarely and higher figures are usually restricted to local concentrations.*

Arsenic. For preliminary work on the determination of arsenic in rocks, see Sandell, " Colorimetric Determination of Traces of Metals," New York, 1944, p. 145.

Cadmium. Sandell (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 264) found Cd of the order of 10^{-5} per cent. in igneous rocks by a dithizone extraction method.

Lead. The determination of lead in radio-active minerals is required in connection with age determinations ; its estimation in rocks is seldom required, but methods are available (Sandell, *Ind. Eng. Chem., Anal. Ed.*, 1939, **9**. 464 ; " Colorimetric Determination of Traces of Metals," New York, 1944, p. 294).

* A. H. Lang. *Canad. Mining and Metall. Bull.*, 1950, No. 460, 426-433.

CHAPTER XII

COMPUTATIONS AS A CHECK ON THE ACCURACY OF CHEMICAL ANALYSES

A. Rock Analyses

For the chemist who has no knowledge of mineralogy and petrology, there are few arithmetical checks which he can usefully apply before returning the results of his analysis, but there will be extremely few exceptions to the following rule : There should be sufficient CaO to make calcite ($CaCO_3$) with the CO_2 plus tricalcium phosphate ($Ca_3(PO_4)_2$) with the P_2O_5. High alumina (for example, 20 per cent. or more) in an igneous rock containing well over 50 per cent. of silica should be confirmed. More often than not it will be due to an error in the separation of alumina and magnesia. There may be other analyses of the same or similar material available for comparison, but beyond these few points the chemist can scarcely go unless he learns (*a*) to calculate the norm, (*b*) to identify minerals and rock types under the microscope and to estimate the relative amounts of the former by micrometric methods.

The geologist, however, has devised several ways of re-calculating analyses for the threefold purpose of classification, interpretation of the rock in terms of standard minerals, and as a check on the accuracy of the chemical analysis. The re-calculation of the chemical analysis of a rock in terms of certain standard minerals, or calculation of the " norm," gives the normative composition of the rock which, although it may often closely resemble the actual or " modal " mineral composition, seldom agrees with anything like mathematical exactness. Nevertheless, the mode and the norm must be compatible from a petrological point of view.

Admittedly the procedure of calculating the norm is of

necessity an arbitrary one, but the results are none the less useful and instructive whether or no the C.I.P.W. classification is adopted. Space does not permit a discussion of the methods of calculating the norm or a description of the C.I.P.W. classification, which is of chemical analyses rather than of igneous rocks. For a detailed description of the calculation of the norm and the subject of interpretation of graphical representation of chemical analyses of rocks and minerals, the reader is referred to Chapter X of Prof. A. Holmes' "Petrographic Methods and Calculations." For a critical discussion of the character, use, and methods of rating rock analyses, see H. S. Washington, *Professional Paper*, 99, *U.S. Geological Survey*, 1917. This last work also contains a classified list of all the chemical analyses of igneous rocks published from 1884-1913 inclusive. Washington, however, was too ready to think that a rock with relatively high water and carbon dioxide was "altered." According to current opinion, these are often genuine magmatic constituents.

There is every reason to encourage the analyst to learn to calculate the norm of an igneous rock and to compare it with the results of an examination of a thin section under the petrological microscope and with analyses of other rocks of similar type. In addition to affording a check on the analytical results, it will give the analyst a growing insight and interest in the implications of his results, tending thereby to eradicate any tedium due to the routine nature of rock analysis.

Before the norm can be adequately computed a sufficient number of constituents must be determined, and for this purpose the usual thirteen specified on p. 28 should be considered a minimum. It is useless to attempt to calculate the norm on rough outline analyses which do not separate iron from alumina or the alkalis from one another. The omission of phosphorus has an important effect, for the P_2O_5 takes a certain amount of CaO to make apatite. In consequence, there is less lime to make anorthite and diopside. If, then, there is no excess of lime after making anorthite, corundum may appear in the norm. The following example shows the effect of P_2O_5 in particular, and to

a lesser extent the effects of MnO and BaO. At A these constituents are omitted; at B they are incorporated in the same analysis. The norms corresponding to these two statements of the same analysis are then compared with the mode, the incorporation of these additional constituents bringing a much closer degree of approximation of the norm to the mode. The effect of the P_2O_5 is to take three times as much CaO to make normative apatite. This reduces the amount of CaO available for anorthite, leaving an increased surplus of Al_2O_3 and SiO_2 to make corundum and quartz. The BaO is added to CaO for purposes of the norm, but in this instance its effect is more than outweighed by the P_2O_5 requiring CaO to make apatite. The MnO is added to FeO which slightly increases the hypersthene. Another effect on the norm is that the available Al_2O_3 is reduced by the amount of P_2O_5 and MnO.

TABLE V.

METADOLERITE, NEAR WAKI CAMP, BUNYORO, UGANDA

Chemical Analysis.	*A.*	*B.*		*Norm of A.*		*Norm of B.*		*Mode.*
SiO_2	51·77	51·77	Quartz	8·28		9·70		9·73
TiO_2	2·42	2·42	Orthoclase	2·22		2·22		
Al_2O_3	17·68	17·03	Albite	19·91	57.99	19·91	55·66	56·31
Fe_2O_3	2·61	2·61	Anorthite	35·86		32·53		
FeO	9·64	9·64	Corundum	0·31		0·82		—
MgO	5·08	5·08	Hypersthene	24·32		24·45		28·18
CaO	7·21	7·21	Iron-ores	8·27		8·27		5·78
Na_2O	2·34	2·34	Apatite	—		1·34		n.d.
K_2O	0·37	0·37	H_2O (Total)	0·81		0·81		
H_2O+	0·44	0·44						100.00
H_2O-	0·37	0·37		99·98		100·05		
P_2O_5	n.d.	0·57						
MnO	n.d.	0·08						
BaO	n.d.	0·05						
	99.93	99.98						

Analyst, A. W. GROVES.

Lime is allotted to carbon dioxide to make calcite, so, if appreciable carbon dioxide is present and has not been determined, the above-mentioned effect on the norm will be accentuated. Iron is allotted to sulphur, so that the

non-determination of an appreciable amount of sulphur also has important repercussions on the norm. The effect of the non-determination of other minor constituents is usually not marked, apart from the exceptional case when there is a considerable amount of the particular constituent present.

Having calculated the norm, the result is compared with the actual or modal composition of the rock. In igneous and metamorphic rocks, when quartz is visible under the microscope, the geologist generally expects to find a comparable amount of free silica or quartz in the norm. Likewise, if there are minerals such as olivine or leucite in the rock, indicating undersaturation with regard to the silica, he expects, with few exceptions, to find this state of affairs reflected in the norm. An excess of alumina or corundum in the norm is to be viewed with suspicion if the petrologist knows that the igneous rock is uncontaminated by sediments and contains no mica. The presence of mica in an ordinary granite or diorite, however, does not as a rule result in more than 2 per cent. of normative corundum. The presence of more than 5 per cent. of normative corundum is usually taken as an indication of a sedimentary origin.

Particularly in the more acid igneous holocrystalline rocks where the constituents of plagioclase do not enter to any appreciable extent into amphibole, the normative composition of the plagioclase should correspond fairly closely to that determined under the microscope by optical methods. Indeed, this agreement is often very close in the acid and intermediate plutonic rocks, becoming gradually more divergent with increased content of modal ferromagnesian minerals, particularly amphiboles and micas. Unless a considerable amount of potash has entered into the constitution of a mica or amphibole, there should be good agreement between normative and modal orthoclase. Likewise the ratio between normative and modal orthoclase to plagioclase should correspond to the modal porportion of these minerals. An exception, apparent rather than real, however, is afforded by the frequent occurrence of untwinned plagioclase in rocks of the charnockite series where as much

as one-third or more of the plagioclase may be devoid of twinning.*

The relative proportions of salic (quartz, felspars, leucite, nepheline, and corundum) to femic minerals (pyroxene, olivine, and accessory minerals) in the norm should agree fairly closely with the relative proportions of their modal counterparts, particularly in the acid and intermediate igneous rocks. With increasing basicity, more and more of the constituents of the anorthite molecule enter the make-up of hornblende and other amphiboles with a corresponding divergence between the norm and the mode. The norm and the mode are seemingly at variance, though the analysis is correct, in many fine-grained and rapidly crystallized lavas and hypabyssal rocks. The main difficulty in such cases is to identify the minerals when in extremely fine crystal meshes. The usefulness of the comparison is largely reduced in the case of rocks containing much glass.

These comparisons can be made roughly by eye, using representative thin sections of the rock under the microscope, but a much closer comparison can be made if a micrometric analysis is available. Such micrometric analyses of all but coarsely porphyritic rocks can be made in an hour or two by means of the Shand recording micrometer* which determines one mineral at a time, or more rapidly still by means of the Leitz integrating micrometer which deals with several minerals at once. In the absence of one or other of these forms of apparatus, a micrometric analysis may be carried out by means of the Rosiwal method (A. Holmes, p. 318), though at the expense of more time. Nevertheless, when the accuracy of an analysis is seriously questioned a micrometric analysis should certainly be made for comparison. It must be borne in mind that a micrometric analysis of the mode or actual mineral composition is inevitably on a volume basis, whereas the normative composition is on a weight basis. Some allowance should be made on this account, though variations due to this cause are usually not marked.

* A. W. Groves, *Q.J.G.S.*, 1935, **91**, 162 and 164.

† A. Holmes, "Petrographic Methods and Calculations," London, 1921, p. 319; S. J. Shand, *J. Geol.*, 1916, **24**, 394.

The following examples of modes with the correspondin; norms illustrate these comparisons :

TABLE VI

NORMS

	A.	B.	C.	D.	E.
Quartz	25·26	13·88	2·40	—	13·80
Orthoclase	23·91	15·01	6·12	0·56	20·02
Albite	24·63	31·44	35·63	14·15	38·77
Anorthite	13·07	21·78	30·02	34·75	10·84
Corundum	1·12	0·64	—	—	—
Diopside	—	—	2·41	25·04	9·93
Hypersthene	10·81	11·66	13·30	5·22	2·32
Olivine	—	—	—	15·68	—
Magnetite	0·46	0·93	7·19	1·86	2·55
Ilmenite	—	2·89	1·82	1·37	0·46
Apatite	—	0·67	2·02	0·34	0·67

MODES

	A.	B.	C.	D.	E.
Quartz	20·3	11·0	1·0	—	18·97
Felspar	58·0	49·0	69·0	30·0	67·25
Hornblende	—	14·3	—	27·6	5·94
Biotite	9·4	—	6·9	—	26·34
Diopside	—	1·6	2·2	16·3	—
Hypersthene	12·3	12·0	15·8	9·3	—
Garnet	—	5·1	—	11·7	—
Ores	—	6·9	5·1	2·7	1·50*

The rocks A, B, C, and D cover a wide silica range among members of the charnockite series of Uganda.†

A is a hypersthene-granite (charnockite proper) with 70 per cent. of silica. The total normative felspar is 61·6 per cent. as against an actual felspar content of 58·0 per cent. The normative hypersthene is slightly less than the modal content, and the small amount of normative magnetite is not represented by any modal magnetite. The surplus iron from these two sources has entered biotite, and the 9·4 per cent. of modal biotite is reflected by the appearance in the norm of 1·12 per cent. of corundum. The formation of this biotite reduces the quartz and alkali felspar of the mode as compared with the norm.

B is a quartz-hypersthene-diorite containing 60 per cent. of silica. The normative quartz at 13·88 per cent. is fairly comparable with the 11·0 per cent. of modal quartz, par-

* Including sphene.

† A. W. Groves, *Q.J.G.S.*, 1935, **91**, 150-207.

ticularly when the other factors are taken into account. There is a considerable difference between the total normative felspar at 68·23 per cent. as compared with the actual felspar content of 49·0 per cent., but this difference is accounted for by the fact that a large proportion of the anorthite molecule has entered the 14·3 per cent. hornblende, 1·6 per cent. diopside, and 5·1 per cent. garnet of the mode, for the modal and normative hypersthene are in complete agreement. The 0·64 per cent. of normative corundum is reflected in the modal garnet. Thus it will be seen that, taking these factors into account, the agreement between norm and mode is satisfactory.

C is a diorite near to norite and contains 52·23 per cent. of silica. There is 71·77 per cent. of normative felspar as against 69·0 actually in the rock. There is close agreement between normative and modal diopside and fair agreement between the two hypersthenes. The excess of normative iron ores over the amount in the mode is due to the fact that these constituents have entered biotite and hypersthene. With only this one disturbing factor the agreement between the normative and modal quartz is quite good.

D is a basic garnetiferous norite of the charnockite series but is also very closely comparable with the Tertiary eucrite of Rum (E. M. Guppy and H. H. Thomas, 1931, analyses 220, 225). The norm shows the rock to be undersaturated with respect to silica and to contain normative olivine. This is in agreement with the absence of quartz from the mode. There is poor agreement with regard to the felspars, the normative felspar totalling 49·46 per cent. and the modal 30·0 per cent. Little agreement is to be found between the two diopsides and hypersthenes, but clearly these differences are due to the fact that the modal composition includes large amounts of the complicated minerals hornblende and garnet to which both salic and femic constituents have contributed. This garnetiferous norite with a silica content of only 47 per cent. is an example of a rock largely composed of minerals far more complicated in chemical composition than those of the norm, with a proportionate disparity between the normative and modal compositions as a result. Nevertheless, as would be expected, there is no modal

orthoclase and the plagioclase is actually labradorite. It is of interest to observe that the Scottish heteromorph is described by H. H. Thomas (*op. cit.*) as being composed of olivine, hypersthene, magnetite, and subordinate biotite, with diallagic augite and bytownite. The mode of this rock, of course, would agree very closely with the norm, the small amount of normative orthoclase representing the subordinate modal biotite.

E is a biotite-hornblende-tonalite from the Kenya-Uganda border (A. W. Groves, *Ann. Rep. Geol. Survey Uganda for* 1931 [1932], p. 16), containing 64·50 per cent. silica. Normative felspar at 69·63 per cent. agrees with modal felspar at 67·25 per cent. There happens to be exact correspondence between the normative and modal ferromagnesians, but whereas the normative minerals are diopside and hypersthene the modal representatives are biotite and hornblende. The biotite is a complex combination of salic and femic constituents. The orthoclase-building material which has entered the biotite requires less silica than in ordinary orthoclase. Similarly, the excess of lime over alumina and the presence of titania have led to the formation of sphene, which also has a lower silica allotment than felspar. If the hornblende happens to be of a type in which some of the silica is replaced by alumina, then this will provide yet another cause for the excess of modal over normative quartz. The low modal iron ore compared with the amount shown in the norm is explained by the fact that most of this iron has entered biotite and hornblende rather than modal iron ore. The excellent agreement in this case is, therefore, less simple than it would at first appear to be, and the more complicated manner of combination of the constituents in nature as compared with the artificial norm explains the apparent discrepancy of over 5 per cent. in the modal and normative quartz.

B. Mineral Analyses

Even before the introduction of X-ray methods of structure analysis of crystals, it was in some favourable cases, an easier matter to check the accuracy of a chemical analysis of a mineral than it was one of a rock. The percentages of

oxides or elements presented in the analysis could be calculated to atomic or molecular ratios and then grouped according to the accepted chemical constitution of the mineral, or according to accepted isomorphous groups. Even when the chemical constitution had not been established, but was nevertheless relatively simple, it was often possible to obtain the formula fairly readily by means of a little arithmetical manipulation. Under those conditions the degree of approximation to integral ratios that could be accepted as satisfactory was, of necessity, quite arbitrary. On the other hand, in cases of more complicated but unknown constitution, there were few limits to the complications that might be introduced into a suggested chemical formula and the evidence on which such a formula rested was of necessity often very inadequate. In such cases an unscrupulous chemist might pass off a bad analysis, but before the reader has finished this chapter he should realize, even if he has not done so previously, that nowadays the career of a bad mineral analyst is likely to be extremely short.

The difficulty formerly experienced in recasting analyses of the amphiboles into some manner conforming to their constitution is brought out by the following quotation from J. P. Iddings' "Rock Minerals" (2nd ed., 2nd impression, 1921, p. 350):

"According to Tschermak, there may be: $CaMg_3(SiO_3)_4$, $Ca(Mg,Fe)_3(SiO_3)_4$, $(Fe,Mg)SiO_3$, $(Fe,Mn,Mg)SiO_3$, $FeSiO_3$, also $((K,Na)_2Mg,Ca,Mn,Fe)SiO_3$, $NaAl(SiO_3)_2$, $NaFe(SiO_3)_2$, together with the hypothetical molecule $(Mg,Fe)(Al,Fe)_2$-(SiO_6). Penfield suggested the general expression: $R''(SiO_3)$, in which R''=Mg, Fe, Ca, (Mn), Na_2, H_2, (Al_2OF_2), (Fe_2OF_2), $(Al_2O(OH)_2)$, $(Fe_2O(OH)_2)$. To this Washington adds $(R_2',R'')R_2'''(SiO_3)_4$."

The introduction of X-ray methods of structure analysis, accompanied by measurement of the actual sizes of the structural units of many minerals, has radically transformed the whole situation so that, in the great majority of cases, not only can a chemical formula for a mineral be assigned with confidence, but conversely the analysis itself can be the more closely scrutinized with almost equal confidence. X-ray methods have revealed even the most complicated

structures and enabled general formulæ to be given for such complex structural groups. Now that these general formulæ have been established, it is possible to work out satisfactory formulæ for some of the most complex silicate minerals such as the amphiboles and micas, with the additional benefit of having a very accurate check on the chemical analysis.

One of the results of this X-ray work has been to show, as explained in Chapter XI, that the elements do not necessarily replace one another solely according to valency and degree of chemical affinity but according to :

(*a*) The size of the ions. The crystal structure can tolerate substitution of some of its component ions by others of approximately similar size (there is a tolerance of about 10 per cent.). Within this degree of tolerance, the rather smaller ions enter more readily than the larger ones.

(*b*) The ionic charge or valency. Substitution of ions of approximately the same size but of different ionic charge can occur, provided that other adjustive substitution of ions can take place at the same time in order to maintain a neutral charge on the lattice.

Among ions within the appropriate size limits, those of larger charge relative to the ions being substituted enter the lattice more easily, and those of smaller charge less easily than the ions being substituted.

Thus in spite of their different valencies, the three elements K, Na, and Ca are able to replace one another. This, incidentally, is reflected in the break between orthoclase and the plagioclases. Likewise trivalent aluminium is able to replace tetravalent silicon, and frequently does so in the amphiboles, whereas in plagioclase evolution directed towards albite silicon displaces aluminium. Another important point to be borne in mind is that X-ray studies of crystal structure have shown how very few minerals are molecular compounds, most, and the silicates in particular, being ionic. The varietalism displayed by, say pyroxenes and amphiboles, micas, etc., is thus largely due to interplay between atoms individually and atom associations. For this reason it is more usual and certainly more accurate and informative

in the case of minerals, to use ionic or atomic formulæ rather than the older molecular formulæ. For an account of this fascinating subject the reader is referred to the following: A. Brammall, *Science Progress*, 1936, **30**, 616-627; *Mineralog. Mag.*, 1936, **24**, 362-366; V. M. Goldschmidt, "Kristallchemie," *Handwörterbuch des Naturwissenschaften*, Jena, 1934, 1128-1154.

Both in preparing mineral samples for analysis and in interpreting the results of analyses, the purity of the sample analysed is of paramount importance. Before analysis the material should be examined under the microscope and the contaminating minerals recognized. It may be possible by treatment with heavy liquids, by centrifuging, or by magnetic or electrostatic methods, to separate some or all of the impurities. Sometimes a chemical treatment can assist as, for example, when an impurity is acid-soluble; but chemical methods have always to be applied with caution for there is often considerable risk of some attack on the mineral it is proposed to analyse. Should the impurity be present as inclusions, or if for any reason it cannot be removed, its quantity may often be calculated and deducted from the analysis. When there is only one contaminating mineral and it has a known definite composition, such an adjustment of the analysis is a simple matter. In this connection a plea is entered for the greater purification of mineral specimens before chemical analysis.

As an example of recalculating a mineral analysis free from an impurity known to be present, we may consider the following analysis of a garnet inseparably mixed with a certain amount of quartz:

TABLE VII

Recalculated to 100.		*Molecular Proportions.*		
SiO_2	52·62	·877	RO_2 ·879 − ·362 = ·517	3
TiO_2	0·17	·002		
Al_2O_3	13·86	·136	R_2O_3 ·172	1
Fe_2O_3	5·80	·036		
MgO	11·50	·2875	RO ·517	3
FeO	14·07	·196		
MnO	0·36	·005		
CaO	1·62	·129		

The general formula (old style molecular formula) for garnet has long been known to be $3RO.R_2O_3.3RO_2$. Inspection of the proportions of RO_2 to R_2O_3 and RO confirms an excess of RO_2, namely silica. The RO is almost exactly three times the R_2O_3, as it should be, and we are therefore justified in excluding a molecular proportion of 0·879 less 0·517, or 0·362, of silica to make the 3 : 1 : 3 ratio. By multiplying this molecular proportion of quartz by 60 (Si=28·5, O_2=32) we get the percentage amount of quartz — *viz.*, 21·7. If necessary, a fair degree of check on this figure could be obtained by means of a micrometric analysis. This incidentally is an old-style calculation on the lines employed before the results of X-ray studies of crystal structure had become generally known and applied to chemical analyses of minerals. Nowadays the composition of the above garnet would be expressed by the formula $(Fe'', Mg, Ca, Mn)_3 (Al, Fe,''' Ti)_2 Si_3 O_{12}$.

The author's analyses of the cobalt-bearing silicate lusakite, at the time a newly discovered mineral from Northern Rhodesia, may be quoted as an example of the effect of the presence of 5 per cent. or so of impurities in a sample submitted for analysis and their effect on the subsequent calculation of the mineral formula. (A. C. Skerl and F. A. Bannister, *Mineralog. Mag.*, 1934, **23**, 598-606.)

The first sample was obtained by crushing the quartz-magnetite-lusakite rock and hand-picking the fragments of lusakite; these, however, carried a certain amount of magnetite and quartz as inclusions. The resulting ratios did not clearly indicate any particular formula for the mineral. The second sample was obtained by powdering rock containing lusakite, quartz, and magnetite, but not kyanite, extracting the magnetite magnetically, and then boiling repeatedly with hydrochloric acid to dissolve any remaining magnetite; the mineral was then separated from quartz by scattering the powder over the surface of bromoform contained in a large funnel and repeating the operation several times. The powder, of which 3·5 g. were used for the analysis, was then as pure as it was possible to obtain it, and the second analysis differed from the first in a lower content of iron oxides and titania (representing about 5 per

TABLE VIII

	I.	*Mol. Ratios.*			*II.*	*Mol. Ratios*		
SiO_2	27·07	0·451			27·23	0·453		
TiO_2	0·80	0·010	0·461	9·75	0·50	0·006	0·459	7·75
Al_2O_3	48·15	0·472			50·72	0·497		
Cr_2O_3 .	trace	—	0·540	11·34	n.d.	—	0·528	8·905
Fe_2O_3 ..	10·83	0·068			4·96	0·031		
FeO . .	2·22	0·031			3·42	0·048		
NiO . .	0·53	0·007			0·89	0·012		
CoO	6·79	0·091	0·189	4·00	8·48	0·113	0·237	4·00
MnO .. .	trace	—			0·08	0·001		
MgO . .	2·44	0·060			2·56	0·063		
CaO ...	nil.	—			nil.	—		
$H_2O + 110°$ C.	1·00	0·056	0·056	1·17	1·19	0·066	0·066	1·11
$H_2O - 110°$ C.	0·35				nil.			
S	0·07				——			
	100.25				100·03			

cent. of titanomagnetite in sample I), relatively lower silica, and a corresponding increase in all the remaining constituents. On totalling oxides of similar valency, a close approximation to the formula $H_2O.4R''O.9Al_2O_3.8SiO_2$ or $H_2R''_4$-$R'''_{18}Si_8O_{48}$ appeared. Bannister's X-ray investigations then showed that lusakite is closely related, structurally, to staurolite, $H_2O.4FeO.9Al_2O_3.8SiO_2$. Bearing in mind, therefore, that the figure for ferrous iron is undoubtedly low on account of the refractory nature of the mineral towards acids, analysis II may be interpreted as a cobaltiferous and nickeliferous staurolite represented by the formula H_2O.-$2(Co,Ni)O.FeO.MgO.9(Al,Fe)_2O_3.8SiO_2$.

The first step in checking the analysis of a mineral is to ascertain its chemical formula, or, if it belongs to a group of complicated minerals, the general formula for the group. Owing to the very rapid progress now being made in this aspect of mineralogy, particular care should be taken to ascertain that recent work has not been overlooked. If a really modern text-book of mineralogy giving these structural formulæ is not available, one of the best means of finding recent information is from the Mineralogical Abstracts published in each number of the *Mineralogical Magazine.*

Let us consider the analysis of an olivine* given in Table

* W. A. Deer and L. R. Wager (*Amer. Min.*, 1939, **24**, 19).

IX. Now the olivines are characterised by single tetrahedra of SiO_4 and can be represented by the general formula $R_2[SiO_4]$. To recast this analysis to an atomic basis, therefore, we require to recalculate the atomic ratios to the basis of 4 oxygens. To achieve this end we adopt the following procedure :

TABLE IX

	Weight per cent.	*Molecular Proportions*	*Atomic Ratios*	*Oxygen Atoms*	*Atomic ratios to 4 oxygens*	
SiO_2	33·72	0·5614	0·5614	1.1228	1·000	
Al_2O_3	nil	—	—	—	—	
TiO_2	trace	—	—	—	—	
Fe_2O_3	0·05	0·0003	0·0006	0·0009	0·001	
FeO	47·91	0·6669	0·6669	0·6669	1·188	1·998
MnO	0·41	0·0058	0·0058	0·0058	0·010	
MgO	18·07	0·4482	0·4482	0·4482	0·799	
CaO	nil	—	—	—	—	
	100·16			2·2446		

$$\frac{4}{2.2446} = 1.78206$$

The analysis itself is given in the usual way in percentages by weight in the vertical column on the left-hand side. In the next column each percentage by weight has been divided by the corresponding molecular weight, so that these are molecular proportions. By multiplying each molecular proportion by the corresponding number of metal atoms present, we get in column 3 the atomic ratios for all the cations. We require now to find a conversion factor by which to multiply the atomic ratios to give unit-cell contents. We know that the unit cell of olivine contains four oxygen atoms and that affords us a basis on which to find the desired factor whereby to convert the analysis to a unit-cell basis. We already have the atomic ratios for the cations, and we want next to ascertain the atomic ratio for oxygen. For this, a formal calculation of the percentage of oxygen is unnecessary ; instead the molecular ratios of the oxides are multiplied by the number of oxygen atoms in each oxide, as is shown in column four. Thus in the case of the sesquioxides one and a half oxygens are contributed, against two in the case of silica, and one in each of the RO oxides. Column four is totalled and

4 divided by this sum gives the required factor. The atomic ratios of column three are then multiplied by this factor giving in column five the atomic ratios on the basis of 4 oxygens. It will be observed that the silica ratio is already the theoretical unity, as it should be in this case since there is no replacement of Si by Al in the independent SiO_4 tetrahedra. Moreover, in this particular structure the replacement of divalent Mg, Fe, and Mn by trivalent Fe and Al or tetravalent Ti does not take place, the olivines having a relatively simple composition. Summation of the remaining constituents, therefore, gives an extremely close approximation to 2·000.

In calculations such as these, use of the approximate molecular weights such as is commonly done in calculations of the norm of a rock, is scarcely good enough. It is advisable to use molecular weights correct to two places of decimals, and, using five figure logarithm tables, to keep to four significant figures, so that in the last column the results are accurate to three places of decimals. A table of molecular weights for this purpose, together with their logarithms, is given in Appendix D.

As an example of a somewhat more complex mineral, we may consider the monoclinic pyroxene set out in Table X; it is an instance of the single chain structure among natural silicates.

In this case the constituents of the chemical analysis have been copied down in an unusual order. The chemical constituents are in fact here arranged in order of effective radius of the elements, so that when the final column on the right-hand side is reached, the atomic ratios are already conveniently grouped in accordance with the general monoclinic pyroxene formula of Machatschki*, *viz.* :—
$XY(Si,Al)_2(O,OH,F)_6$ in which X=Ca, Na, (K), (Mn), (Mg), and Y=Mg, Fe, Mn, Al, (Zn), (Ti). It will also be observed that although $H_2O+105°$ C. and $H_2O-105°$ C. are retained in the analysis, only the former is utilized in the calculation. This is because in mineral analyses it is usual to assume that H_2O+ represents hydroxyl water, an essential part of the crystal lattice, whereas H_2O- represents merely adsorbed

* *Zeits. Krist.*, 1929, **71**, 219-236.

TABLE X.

	*Weight per cent.**	*Molecular Proportions*	*Oxygen Atoms*		*Atomic Ratios*	*Atomic ratios on basis 6 (O, OH, F)*	
SiO_2	54·23	0·9026	1·8052	Si	0·9026	1·967	2.00
Al_2O_3	1·84	0·0181	0·0543	Al	0·0362	0·033	
						0·047	
TiO_2	0·14	0·0018	0·0036	Ti	0·0018	0·004	1.01
Fe_2O_3	0·92	0·0058	0·0174	Fe‴	0·0276	0·025	
Li_2O	0·02	0·0007	0·0007	Li	0·0014	0·003	
MgO	16·02	0·3973	0·3973	Mg	0·3973	0·865	
FeO	1·98	0·0276	0·0276	Fe″	0·0276	0·060	
MnO	0·23	0·0032	0·0032	Mn	0·0032	0·007	
Na_2O	0·88	0·0142	0·0142				
CaO	24·02	0·4273	0·4273	Na	0·0284	0·062	1.00
K_2O	0·03	0·0003	0·0003	Ca	0·4273	0·933	
H_2O+	0·04	0·0022	0·0022	K	0·0006	0·001	
H_2O-	0·05	—	—	OH	0·0044	0·010	6.00
F	trace	—	—	O	—	5·990	
Cl	trace	—	—				
	100·40		2·7533		$\frac{6}{2·7533}$ = 2·1792		

Valency Check

	+	—	—
Si++++	7·872	OH	0·010
Al+++	0·237		
Ti++++	0·016	O	11·980
Fe+++	0·075		11·990
Fe++	0·120		
Mg++	1·730		
Ca++	1·866		
Mn++	0·014		
Li++	0·003		
Na+	0·062		
K+	0·001		
	11·996		

Analyst. C. O. Harvey.

moisture. [This is not always strictly the case, *e.g.*, among the micaceous clay minerals it is usual to distinguish between adsorbed interlayer water between the lattice sheets and the so-called high-temperature water, or rather hydroxyl, which is an essential part of the crystal lattice.] Further, had any F′ or Cl′ been present in this analysis, the oxygen equivalent for these would have been subtracted from the sum of the oxygen atoms before arriving at the factor. This, however, is further explained in the example of an amphibole given

* A. F. Hallimond, *Mineralog. Mag.*, 1947, **28**, 234-236.

later.

In accordance with the general monoclinic pyroxene formula, the atomic ratios have been calculated to a basis of 6 oxygens. It should be pointed out that the figure given for the atomic ratio of oxygen is simply derived, as a last step, by subtracting the hydroxyl ratio from 6. It will be observed that Si is just short of 2. The Al figure is therefore divided so that 0·033 goes with the Si to make it up to 2 while the remainder goes in the Y or Mg group. The X or (Ca, Na) group is very close to 1 atom. There is a small replacement of Ca by Na. This, then, is a fairly pure diopside. Chemical analyses of monoclinic pyroxenes do not always come out so near the theoretical when treated in this way. A more marked deficiency in the (Ca, Na) coupled with an excess in the Mg group is often due to the presence of a little of the orthorhombic pyroxene, enstatite, which is sometimes apt to develop in parallel growth with monoclinic pyroxene, making a clean separation of these two minerals extremely difficult. From this we may correctly deduce that marked divergence from the theoretical result of a known mineral usually indicates either a bad analysis or that the chemist has not been given a pure mineral to analyse. In the latter case, however, the application of optical methods (either by transmitted light, or, in the case of opaque minerals, by polished surfaces) or X-ray methods will show whether the blame lies with the chemist or the mineralogist. Failure to attain integral relations does not always indicate an inaccurate analysis, especially when there is a deficiency. Vacant lattice positions have been found to be of comparatively frequent occurrence. An excess, however, is much more likely to indicate an error.

As a final example, we will take an analysis of a hornblende from the same paper by A. F. Hallimond.

The analysis (of a pargasite from the Tiree marble) is written down (see Table XI) with the constituents arranged in order of effective radius. H_2O- is listed for completeness, but is not used in the calculation. (A trace of P_2O_5 was also recorded in the analysis.) On reaching the bottom of the column of oxygen atoms, it will be noted that fluorine and chlorine have been given a half value. This is because in

TABLE XI

	Weight per cent.	Molecular Proportions	Oxygen Atoms		Atomic Ratios	Atomic Ratios on Basis 24 (O, OH, F)	
SiO_2	41·72	0·6947	1·3894	Si	0·6947	6·154	8.00
Al_2O_3	15·86	0·1556	0·4668	Al	0·3112	1·846	
						0·918	5·26
TiO_2	0·81	0·0101	0·0202	Ti	0·0101	0·089	
Fe_2O_3	3·36	0·0210	0·0630	Fe‴	0·0420	0·372	
Li_2O	0·02	0·0007	0·0007	Li	0·0014	0·012	
MgO	14·14	0·3507	0·3507	Mg	0·3507	3·108	
FeO	6·03	0·0839	0·0839	Fe″	0·0839	0·743	
MnO	0·12	0·0017	0·0017	Mn	0·0017	0·015	
Na_2O	1·42	0·0229	0·0229				
CaO	12·92	0·2304	0·2304	Na	0·0458	0·406	2.94
K_2O	2·60	0·0276	0·0276	Ca	0·2304	2·041	
H_2O+	0·85	0·0472	0·0472	K	0·0552	0·489	
F	0·16	0·0084	0·0042				
Cl	0·46	0·0013	0·0006	OH	0·0944	0·836	24·00
H_2O-	0·04			F	0·0084	0·074	
			2·7093	Cl	0·0130	0·124	
	100·51			O	—	22·966	
Less O for F, Cl	0·17						
	100·34						

$$\frac{24}{2{\cdot}7093} = 8{\cdot}8589$$

Valency Check

	+		—
Si++++	24·616	OH^-	0·836
Al+++	4·146	F^-	0·074
Ti++++	0·354	Cl^-	0·124
Fe+++	1·116	O^{--}	45·932
Fe++	1·486		46·966
Mg++	6·214		
Ca++	4·082		
Mn++	0.020		
Li+	0·012		
Na+	0·406		
K+	0·489		
	47·087		

Analyst : C. O. Harvey.

the mineral, fluorine and chlorine atoms are linked with either a metal or hydrogen, so that for each two fluorine atoms only one additional oxygen atom has been introduced into the analysis. (For the same reason we always deduct the oxygen equivalent of fluorine, chlorine, or sulphur from the summation of an analysis.)

B. E. Warren* has given the following general formula for monoclinic amphiboles :—
$(OH,F)_2$ $(Na,Ca,K)_{2\text{-}3}$ $(Mg,Fe'',Fe''',Ti,Mn,Al)_5$ $[(Si,Al)_8O_{22}]$.
It will be observed that there are 24 (O,OH,F) atoms to the unit cell and so the analysis is computed to this basis. The atomic ratio of oxygen in the last column is obtained by subtracting the sum of the atomic ratios of OH, F, and Cl, (calculated on a basis of 24(O,OH,F)) from 24. Likewise the oxygen in the valency check is derived from this figure.

This analysis when calculated to atomic ratios on this basis and compared with Warren's formula shows almost exactly two atoms of Ca, and the alkali, in which K slightly predominates over Na, fills the ' vacant space ' but does not replace Ca. The replacement of nearly two atoms of Si by Al shows that this process has gone almost to the normal limit. The amphibole under consideration, may now be expressed by the formula :—
$(OH,F,Cl)_{1\cdot 03}(Ca,Na,K)_{2\cdot 94}(Mg,Fe,Ti,Al,Mn)_{5\cdot 26}(Si,Al)_{8\cdot 00}O_{22\cdot 97}$

Having thus learned the method of computing chemical analyses of silicate minerals to atomic ratios on an arbitrary basis the reader must note that *it is always essential to specify the basis assumed.* He should also note that the valency check given in Tables X and XI, where the anionic and cationic charges or valencies are totalled and compared, is not a check on the accuracy of the chemical analyses, the balance of charges being an arithmetical necessity of the calculation itself, and that failure to balance within small limits merely indicates mistakes in the calculations. The valency check is, nevertheless, a worth-while procedure, for evidence of balance is evidence of accurate calculation.

Given a chemical analysis of an unknown silicate mineral, it is often possible by a partial reversal of the method of calculation just demonstrated, first to place the mineral represented in its correct mineral group and then to determine its species still more precisely by comparison with analyses of that group. Stated briefly, the procedure is as follows : The analysis is converted to molecular proportions, and these are converted into atomic proportions

* *Zeits. Krist.*, 1930, **72**, 493-517.

for all the cations. These are multiplied by the equivalent valencies for each atom. Then the sum of the positive metal valencies less the negative OH and F valencies must be equal to the negative oxygen valencies corresponding to the atomic proportions, and half this valency difference (oxygen being divalent) gives the corresponding oxygen atoms. The ratio of O to OH+F is then examined. If there is no OH+F, the single tetrahedron (olivines, etc.) double tetrahedron, or SiO_2 (quartz, felspars, etc.) groups are indicated. If the proportion of O to OH+F is 10 : 2, the micas, chloritoids, or three-layer clay minerals are suggested. If the ratio is 10 : 8, the mineral may belong to the chlorites or two-layer clay minerals. Having decided on the likely type, a factor is then obtained by dividing the number of O+OH atoms of that type by the number of oxygen atoms obtained for the unknown mineral. Bearing in mind that the anions of the two-layer clays, serpentine and amesite total 18, those of the amphiboles, micas, chloritoids, three-layer micas, and talc total 24, and those of the chlorites total 36, the factor, if any of those types are involved, will be obtained by dividing one of these three numbers by the number of oxygen atoms obtained. Multiplying the atomic proportions that were obtained by this factor gives the atomic proportions for the formula sought for the unknown mineral. With the mineral formula thus derived, it should be possible in the case of most rock-forming minerals, to specify the mineral.

Whenever an accurate determination of the density and X-ray measurements of the unit-cell size have been made on the actual material analysed, calculation to empirical unit-cell contents can be made (instead of to atomic ratios to a more or less arbitrary basis as in the examples here presented). The presentation then involves no assumptions and carries the greatest conviction, especially when a new chemical formula is being proposed. For an excellent discussion on the presentation of chemical analyses of minerals in general, and especially in relation to allied X-ray data, the reader is referred to a paper by Dr. M. H. Hey (*Mineralog. Mag.*, 1939, **25**, 402-412).

The clay minerals constitute an exceptionally difficult

group with numerous problems of their own which are best appreciated by studying the following papers: "Calculating formulas for fine grained minerals," by W. P. Kelley, *Amer. Mineralogist*, 1945, **30**, 1-26; "Minerals of the Montmorillonite group," by C. S. Ross and S. B. Hendricks, U.S. Geol. Survey Prof. Paper 205-B, 1945, pp. 23-79.

Before leaving the subject of the calculation of chemical analysis of minerals, reference should be made to a method that was formerly in general use, *viz.*, the calculation, particularly of the more complex silicate minerals, to two or more end-members of an isomorphous group. Thus garnets were calculated to proportions of the following end-groups (among others): grossularite, $Ca_3\ Al_2\ (SiO_4)_3$; pyrope, $Mg_3\ Al_2\ (SiO_4)_3$; almandine, $Fe_3\ Al_2\ (SiO_4)_3$; spessartite, $Mn_3\ Al_2\ (SiO_4)_3$; andradite, $Ca_3\ Fe_2\ (SiO_4)_3$. Or to take a simple case, the orthorhombic pyroxenes were calculated to enstatite ($MgSiO_3$) and hypersthene ($FeSiO_3$). In view of the fact that X-ray studies have shown very few minerals to be molecular, most being ionic, the presentation of these ionic compounds in terms of isomorphous end-members loses physical significance. This is particularly true of the silicates, where the anion is in many cases a chain or net structure co-extensive with the crystal. This method of presentation, however, is still followed where, as in the case of some of the more complex silicates, it affords a purely formal presentation particularly suited to correlation graphs of optical and other physical properties. Thus R. E. Stevens in a paper entitled "A system for calculating analyses of mica and related minerals to end members"* claims that "Complex compositions can be given in percentages of relatively simple end-member formulas, and all such simple formulas that satisfy the chemical and structual requirements of a mica can now be devised. Some of these end-member formulas express compositions of known micas, others may be considered as referring to micas existing only in solid solution with other micas, and many of the formulas express compositions not yet found, many of which may remain hypothetical. With

* "Contributions to Geochemistry, 1942-45." *U.S. Geol. Surv. Bull.* 950, 1946.

such a set of end-member formulas a chemical analysis of a mica may easily be calculated to percentages of the end members. These percentages may be found useful in correlating optical and physical properties. The system of end members also may serve as a basis for classifying members of the mica group . . . . . An expression of an analysis as percentages of end-member formulas means that the various end-member compositions either may be present as discreet particles in an impure sample or they may form a solid solution in a pure mineral. The purity of the sample must be considered and this has been done in most mineral analyses, so that the end-member compositions may be thought to be in solid solution. In a solid solution the end members lose their identity as separate minerals, their ions being in random arrangement in the structure in positions with proper co-ordination for the ion considered."

TABLE XII

OCCURRENCE OF THE MINOR AND RARER CONSTITUENTS IN ROCK-FORMING MINERALS

Element to be Sought	Titanium	Manganese	Phosphorus	Carbon Dioxide	Barium	Strontium
Minerals containing the element as an essential constituent	Rutile Anatase Brookite Ilmenite Leucoxene Sphene Perovskite Geikielite Schorlomite Kaersutite Ivaarite Euxenite Polycrase Rinkalite Dysanalyte Pseudobrookite Titanaugite Pyrochlore Benitoite	Rhodochrosite Pyrolusite Psilomelane Braunite Spessartite Rhodonite Tephroite Franklinite Manganite Schizolite Babingtonite Låvenite Piedmonite Thulite Manganocalcite Jacobsite	Apatite Monazite Xenotime Wavellite Chalcosiderite Amblygonite Turquoise Torbernite Autunite Vivianite Beryllonite Triplite Triploidite Lazulite Fermorite	Calcite Aragonite Dolomite Magnesite Ankerite Siderite Calamine Witherite Strontianite Barytocalcite Strontiano-calcite Cancrinite Scapolite Malachite Azurite Rhodochrosite Bromlite Manganocalcite	Barytes Witherite Hyalophane Celsian Oellacherite Barytocalcite Harmotome Bromlite Benitoite Edingtonite Paracelsian	Celestite Strontianite Rinkolite Strontiano-calcite Fermorite
Groups and species often containing appreciable amounts of the element	Titanomagnetite Biotite Pyroxenes Amphiboles Garnets (especially melanite)	Columbite- Tantalite Tapiolite Many ferro-magnesian silicates			Micas	Micas (especially Biotite) Felspars Aragonite Anhydrite
Present as inclusions	of rutile in chlorite, biotite, etc.		of apatite in quartz, felspar, and ferromagnesian silicates	in quartz, etc.		

TABLE XII.—*Continued*

OCCURRENCE OF THE MINOR AND RARER CONSTITUENTS IN ROCK-FORMING MINERALS

Elements to be Sought	Fluorine	Chlorine	Sulphur	Zirconium	Chromium	Vanadium
Minerals containing the element as an essential constituent	Fluor Topaz Chondrodite Humite Clinohumite Fluor-apatite Cryolite Phlogopite Zinnwaldite Lepidolite Amblygonite Leucophanite Meliphanite Vesuvianite Apophyllite Fermorite	Scapolite Marialite Meionite Chlor-apatite Sodalite Nosean Ameletite Halite (rock salt)	Native sulphur Pyrite Marcasite Chalcopyrite Pyrrhotite Molybdenite and other sulphides Barytes Gypsum Celestite Epsomite Alunite Natroalunite Haüyne Nosean Lazurite	Zircon Baddeleyite Eudialyte Rosenbuschite Låvenite	Chromite Picotite Fuchsite Stichtite Uvarovite Tawmawite Kammererite Kochubeite	Roscoelite Carnotite
Groups and species often containing appreciable amounts of the element	Amphiboles Muscovite Biotite Sphene		Scapolite	Acmite Aegirine-augite	Amphiboles Pyroxenes	Ilmenite Micas Amphiboles Pyroxenes
Present as inclusions	of fluorspar	of rock salt in felspars and quartz	of pyrite	of zircon, common in acid rocks		

TABLE XII.—*Continued*

OCCURRENCE OF THE MINOR AND RARER CONSTITUENTS IN ROCK FORMING MINERALS

Element to be Sought	Nickel	Beryllium	Rare Earths	Boron	Lithium
Minerals containing the element as an essential constituent	Niccolite Millerite Garnierite	Beryl Chrysoberyl Euclase Phenakite Beryllonite Gadolinite Helvite Leucophanite Meliphanite Eudidymite Herderite	Monazite Allanite Xenotime Cerite Yttrotantalite Samarskite Euxenite Polycrase Fergusonite Gadolinite Pyrochlore Koppite Microlite	Tourmaline Axinite Datolite Danburite Dumortierite Serendibite Borax Colemanite Boracite Kernite (Razorite)	Lepidolite Zinnwaldite Amblygonite Spodumene Petalite Triphylite Lithiophylite
Groups and species often containing appreciable amounts of the element	Pyrrhotite Pyrite Many ferro-magnesian silicates Serpentine	Vesuvianite			Tourmaline Beryl (sometimes contains caesium)
Present as inclusions					

APPENDICES

APPENDIX A

Factors

Consituent.	*Sought.*	*Found.*	*Factor.*
Baria	BaO	$BaSO_4$	0·66
Baria	BaO	$BaCrO_4$	0·61
Carbon	C	CO_2	0·27
Ceria	Ce_2O_3	CeO_2	0·95
Chlorine	Cl	$AgCl$	0·246
Copper	CuO	Cu	1·25
Fluorine	F	CaF_2	0·49
Iron oxides	FeO	Fe_2O_3	0·8998
Iron oxides	Fe_2O_3	FeO	1·1113
Lithia	Li_2O	Li_2SO_4	0·27
Magnesia	MgO	$Mg_2P_2O_7$	0·3621
Magnesia	MgO	$Mg(C_9H_6NO)_2$*	0·1291
Manganous oxide	MnO	Mn_3O_4	0·93
Manganous oxide	Mn_3O_4	MnO	1·08
Nickel oxide	NiO	$NiC_8H_{14}O_4N_4$†	0·258
Phosphorus pentoxide	P_2O_5	$Mg_2P_2O_7$	0·6379
Potash	KCl	$KClO_4$	0·5381
Potash	K_2O	KCl	0·6317
Potash	KCl	K_2PtCl_6	0·3067
Potash	K_2O	K_2PtCl_6	0·1938
Soda	Na_2O	$NaCl$	0·5303
Strontia	SrO	$SrSO_4$	0·56
Sulphur	S	$BaSO_4$	0·1374
Sulphur trioxide	SO_3	$BaSO_4$	0·343
Vanadium oxide	V_2O_5	V_2O_3	1·2
Zirconia	ZrO_2	ZrP_2O_7	0·43

* Magnesium quinolate. † Nickel dimethylglyoxime.

APPENDIX B

Specimen Calculation of Analysis of Granophyric Quartz-Diabase, Ivy Scar Rock, Malverns

Main Portion :

Cruc. 181 and rock	=36·1029	
Cruc. 181 alone	=35·1029	
Amount of rock taken	= 1·0000	
Cruc. 181 + x + SiO_2	=35·6179	
,, 181 + x less SiO_2	=35·1065	
SiO_2	= 0·5114	SiO_2 = 51·44%.
Cruc. 181 + R_2O_3	=35·4074	
,, 181 alone	=35·0959 (after removal of melt)	
R_2O_3	= 0·3115 (including x)	
Less blank for HF	= 0·0030	
	0·3085	R_2O_3 = 30·85 %.
Cruc. 236 + CaO	=23·9706	
,, 236 alone	=23·8980	
CaO + SrO	= 0·0726	CaO + SrO = 7·26 %.
Cruc. 236 + $Mg_2P_2O_7$	=24·0243	
,, 236 alone	=23·8971	
$Mg_2P_2O_7$	= 0·1272	MgO = ·1272 × ·3621 = 4·61 %.

Alkalis :

Watch glass and rock	=13·6614	
,, ,, alone	=12·8614	
Rock	= 0·8000	
Dish 228 + NaCl + KCl	=20·7954	
,, 228 alone	=20·7238	
NaCl + KCl + (LiCl)	= 0·0716	
Glass filter-crucible + $KClO_4$	=13·2005	
,, ,, ,, alone	=13·1758	
$KClO_4$	= 0·0247	
	KCl = ·0247 × ·5381	= ·0133
	Less KCl blank of $CaCO_3$	·0013
		·0120
NaCl = ·0716 − ·0133	= 0·0583	
Less NaCl blank of $CaCO_3$	0·0031	
	0·0552	

$$Na_2O\ (+Li_2O) = \frac{\cdot 0552 \times \cdot 5303 \times 100}{\cdot 8} = 3{\cdot}66\ \%.$$

$$K_2O = \frac{\cdot 0120 \times \cdot 6317 \times 100}{\cdot 8} = 0{\cdot}95\ \%.$$

Lithium Test. Nil.

Ferrous Iron :

Cruc. 181 + rock = 36·0937
,, 181 alone = 35·0955

Amount of rock taken = 0·9982

This required 10·1 c.c. of standard $KMnO_4$ (1 c.c. = ·007285 g. FeO).

$$FeO = \frac{10{\cdot}1 \times \cdot 007285 \times 100}{\cdot 9982} = 7{\cdot}37\ \%.$$

Fe_2O_3 equivalent = 7·37 × 1·11 = 8·18 %.

Total Iron : Solution after pyrosulphate fusion of R_2O_3 required 16·9 c.c. of standard $KMnO_4$ (1 c.c. = ·008085 g. Fe_2O_3).

$$\text{Total iron as } Fe_2O_3 = \frac{16{\cdot}9 \times \cdot 008085 \times 100}{1{\cdot}0} = 13{\cdot}67\ \%.$$

Actual Fe_2O_3 in rock = 13·67 − 8·18 = 5·49 %.

Titania : Solution made up to 500 c.c. 50 c.c. required 2·5 c.c. TiO_2 solution (1 c.c. = ·001006 g. TiO_2).

$$TiO_2 = \frac{2{\cdot}5 \times 10 \times \cdot 001006 \times 100}{1{\cdot}0} = 2{\cdot}52\ \%.$$

Hygroscopic Water :

Watch glass and rock = 15·4362	W. g. and rock (1) = 15·4362
,, ,, alone = 12·8614	,, ,, ,, (2) = 15·4319
Amount of rock taken = 2·5748	H_2O − 110° C. = 0·0043

$$H_2O - 110^\circ\ C. = \frac{\cdot 43}{2{\cdot}5748} = 0{\cdot}17\ \%.$$

Total Water :

Silica boat and rock = 7·8368	Absorption tube (2) = 48·7441
,, ,, alone = 5·0752	,, ,, (1) = 48·6766
Amount of rock taken = 2·7616	H_2O = 0·0675
	less blank 0·0035
	0·0640

$$\text{Total } H_2O = \frac{6{\cdot}40}{2{\cdot}7616} = 2{\cdot}32\ \%.$$

H_2O + 110° C. = 2·32 − 0·17 = 2·15 %.

Phosphorus :

Dish 76 + rock = 21·9937	Cruc. 42 + $Mg_2P_2O_7$ = 22·6768
,, 76 alone = 20·4174	,, 42 alone = 22·6581
Amount of rock taken = 1·5763	$Mg_2P_2O_7$ = 0·0187

$$P_2O_5 = \frac{1{\cdot}870 \times {\cdot}6379}{1{\cdot}5763} = 0{\cdot}76\ \%.$$

Manganese and Barium :

Dish 76 + rock = 22·5236
,, 76 alone = 20·4174

Amount of rock taken = 2·1062

Solution made up to 1 litre.

100 c.c. required 1·6 c.c. *N*/50 $KMnO_4$ (1 c.c. = ·0003134 g. MnO).

$$MnO = \frac{1{\cdot}6 \times 10 \times {\cdot}0003134 \times 100}{2{\cdot}1062} = 0{\cdot}24\ \%.$$

Mn_3O_4 equivalent = 0·24 × 1·08
= 0·26 %.

Cruc. 44 + $BaSO_4$ = 22·4664
,, 44 alone = 22·4643

$BaSO_4$ = 0·0021

$$BaO = \frac{{\cdot}21 \times {\cdot}66}{2{\cdot}1062} = 0{\cdot}07\ \%.$$

Strontia :

Cruc. 42 + $SrSO_4$ = 22·6611
,, 42 alone = 22·6582

$SrSO_4$ = 0·0029

SrO = ·29 × ·56 = 0·16 %.

Readily checked spectroscopically. Strontium could even be seen against sodium in the flame test. Practically free from lime.

Carbon dioxide :

Flask and rock = 54·4500
,, alone = 52·4436

Amount of rock taken = 2·0064

1st absorption tube (2) = 46·1542	2nd absorption tube (2) = 36·8879
,, ,, ,, (1) = 46·1533	,, ,, ,, (1) = 36·8879
CO_2 = 0·0009	CO_2 = 0·0000

$$CO_2 = \frac{{\cdot}09}{2} = 0{\cdot}04\ \%\ \text{(blank negligible)}.$$

Nickel :

In dish 111 : specimen tube (1) = 30·1761
" " (2) = 27·1852

Amount of rock taken = 2·9909 No trace of Ni dimethyl-glyoxime.

Fluorine :

Cruc. 181 + rock = 37·1220
" 181 alone = 35·0918

Amount of rock taken = 2·0302

Colour ratio, using 3 c.c. conc. H_2SO_4 = ·70—*i.e.* ·0008 g. F.

$$\therefore F = \frac{\cdot 08}{2{\cdot}0302} = 0{\cdot}04\ \%.$$

Copper Oxide :

In dish 111. Specimen tube (1) = 20·0760
" " (2) = 17·5475

Amount of rock taken = 2·5285

Filtrate from 1st pptn. $\frac{1}{5}$ rqd. 3·0 c.c. Cu soln.* CuO =

$$\frac{15 \times 1{\cdot}252 \times 100 \times \cdot 00001}{2{\cdot}5285} = \cdot 008\ \%.$$

Filtrate from 2nd pptn. $\frac{1}{5}$ rqd. 2·4 c.c. Cu soln.* CuO =

$$\frac{12{\cdot}0 \times 1{\cdot}252 \times 100 \times \cdot 00001}{2{\cdot}5285} = \cdot 005\ \%.$$

Filtrate from 3rd. pptn. $\frac{1}{5}$ rqd. 1·0 c.c. Cu soln.* CuO =

$$\frac{5 \times 1{\cdot}252 \times 100 \times \cdot 00001}{2{\cdot}5285} = \cdot 002\ \%.$$

Total CuO = ·016 %.

Chromium and Vanadium :

Watch glass and rock = 17·7674
" " alone = 12·8614

Amount of rock taken = 4·9060

The whole solution required 1·2 c.c. standard chromium solution (1 c.c. = ·00012 g. Cr_2O_3).

$$Cr_2O_3 = \frac{1{\cdot}2 \times \cdot 00012 \times 100}{4{\cdot}9060} = 0{\cdot}003\ \%.$$

1·9 c.c. $N/50$ $KMnO_4$ required in titration for V_2O_3.

$$V_2O_3 = \frac{1{\cdot}9 \times \cdot 0015 \times 100}{4{\cdot}9060} = 0{\cdot}06\ \%.$$

V_2O_5 equivalent = 0·07 %.

* Containing ·00001 g. Cu per c.c.

Sulphur and Zirconia :

Cruc. 181 + rock = 37·1868	Cruc. 42 + $BaSO_4$ = 22·6648
,, 181 alone = 35·1177	,, 42 alone = 22·6589
Amount of rock taken = 2·0691	$BaSO_4$ = 0·0059
	Less blank = 0·0044
	0·0015

$$S = \frac{\cdot 15 \times \cdot 1374}{2\cdot 0691} = 0\cdot 01\ \%.$$

Zirconia (on residue from S). Nil.

Chlorine :

Watch glass and rock = 15·0420
,, ,, alone = 12·8614

Amount of rock taken = 2·1806

This required 0·5 c.c. of standard NaCl solution (1 c.c. = ·0006 g. Cl) in a turbidimetric comparison.

$$Cl = \frac{\cdot 5 \times \cdot 0006 \times 100}{2\cdot 1806} = 0\cdot 01\ \%.$$

Alumina = 30·85 — 13·67 Fe_2O_3
2·51 TiO_2
0·83 $P_2O_5 + V_2O_5$
0·26 Mn_3O_4 (Holt and Harwood method)

17·27

= 13·58 %.

Oxygen equivalent of	S	·005 approx.
,, ,,	Cl	·002 ,,
,, ,,	F	·02 ,,
		·03

APPENDIX C

Statement of Analysis: Granophyric Quartz-Diabase, Ivy Scar Rock, Malvern Hills

SiO_2	51·47
TiO_2	2·51
Al_2O_3	13·58
Fe_2O_3	5·49
FeO	7·37
MnO	0·24
MgO	4·61
CaO	7·10
Na_2O	3·66
K_2O	0·95
P_2O_5	0·76
$H_2O + 110°$ C.	2·14
$H_2O - 110°$ C.	0·17
CO_2	0·04
ZrO_2	none
F	0·04
Cl	0·01
S	0·01
Cr_2O_3	0·003
V_2O_3	0·06
NiO	none
BaO	0·07
SrO	0·16
CuO	0·016
Li_2O	none
	100·46
O	0·03
	100·43

APPENDIX D

Molecular Weights and their Logarithms for Calculation of Mineral Analyses to an Atomic Basis

	Molecular Weight	*Logarithm*		*Molecular Weight*	*Logarithm*
SiO_2	60·06	1·77858	S	32·06	1·50595
Al_2O_3	101·94	2·00827	FeS_2	119·96	2·07914
Fe_2O_3	159·68	2·20333	Fe_7S_8	647·36	2·81119
FeO	71·84	1·85643	Cr_2O_3	152·02	2·18190
MgO	40·32	1·60552	V_2O_3	149·90	2·17588
CaO	56·08	1·74881	NiO	74·69	1·87326
Na_2O	61·994	1·79235	CoO	74·94	1·87471
K_2O	94·192	1·97401	BaO	153·36	2·18570
H_2O	18·016	1·25565	SrO	103·63	2·01545
TiO_2	79·90	1·90255	CuO	79·57	1·90076
P_2O_5	142·04	2·15214	SnO	134·70	2·12935
MnO	70·93	1·85084	PbO	223·21	2·34871
CO_2	44·01	1·64355	ZnO	81·38	1·91051
ZrO_2	123·22	2·09068	Li_2O	29·880	1·47540
B_2O_3	69·64	1·84286	C	12·01	1·07953
SO_3	80·06	1·90341	H	1·0080	0·00339
Cl	35·457	1·54970	Rb_2O	186·96	2·27177
F	19·000	1·27875	Cs_2O	281·82	2·44996

(Based on International Atomic Weights, 1943)

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